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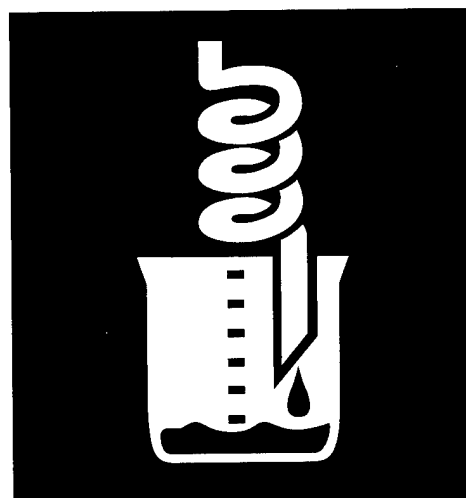
# **The Effect of Fulvic Acid on the Sorption of Lead by Clay Materials**

by  
Brian Foy and Deborah R. Curtin

Sixty-five percent of Army housing units are more than 25 years old and are likely to have surfaces painted with lead-based paint. Lead-contaminated structures require remediation to meet current regulatory mandates and to ensure a safe living environment. Once lead is removed, abatement waste must be disposed in an environmentally responsible manner.

Lead-based paint removed during abatement may contaminate groundwater with excessive lead levels if improperly disposed. Proper site selection for the pollutant disposal and the use of liners are the primary techniques currently available for minimizing the potential for groundwater contamination. Investigation of lead mobility in soil, and the variables that affect its leachability are needed to minimize future contamination of water supplies and to avoid the high expenses associated with remediation.

This study investigated fulvic acid, one parameter that affects the transport of lead in the subsurface. Laboratory bench tests indicated that the sorption of lead on clay materials was enhanced by the presence of fulvic acid. This study also recommends that these results not be used in isolation, without accounting for the many other parameters that may also affect the movement of lead in the subsurface.



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## Foreword

This study was conducted for the Directorate of Military Programs, Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162720A896, "Environmental Quality Technology"; Work Unit UL-T05, "Lead-Based Paint Hazardous Waste Control Technology." The technical monitor was Malcolm McLeod, CECPW-ES.

The work was performed by the Troop Installation Operation Division (UL-T) of the Utilities and Industrial Operations Laboratory (UL), U.S. Army Construction Engineering Research Laboratories (USACERL). The USACERL principal investigator was Deborah Curtin. Part of this work was performed under contract by Dr. John Pfeffer, of the University of Illinois, Urbana-Champaign. Bernard A. Donahue is Acting Chief, CECER-UL-T and John T. Bandy is Operations Chief, CECER-UL. Gary W. Schanche, CECER-UL, is the associated Technical Director. The USACERL technical editor was William J. Wolfe, Technical Resources.

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# 1 Introduction

## Background

### *United States*

Lead is an integral part of the U.S. economy. Approximately 1.3 million tons of lead are consumed by U.S. industry annually. Of that amount, about 600,000 tons are released into the environment by various end uses (Cheremisinoff 1993). Mining, manufacturing, and recycling also emit lead into the environment. The United States is contaminated with lead well above natural background levels, at elevated concentrations that have resulted in a national health hazard. Some experts have concluded that "the detrimental problems associated with lead are currently considered more serious than the asbestos problem" (Cheremisinoff 1993).

The use of lead as a pigment in paint is considered a significant threat to public safety and welfare, and has been the focus of recent government legislation. Concern over health hazards associated with lead-based paint has been growing, especially as those hazards relate to childhood lead-poisoning. Child blood lead levels in excess of 15 mg/dL indicate that the child has been exposed to potentially harmful quantities of lead. The U.S. Agency for Toxic Substances and Disease Registry released the following estimates in 1988:

- From 3 to 4 million children are sufficiently exposed to lead from all sources to elevate their blood lead levels above 15 mg/dL.
- Between 4 and 5 million tons of lead-based paint is dispersed throughout 42 million homes nationwide.
- 13.6 million children under the age of 7 live in housing with potentially toxic levels of lead-based paint; 5.9 million of those children live in the oldest housing with the highest lead content.
- 1.2 million children are sufficiently exposed to lead-based paint to increase their blood lead levels approximately 15 mg/dL.

Lead poisoning resulting from lead-based paint exposure can only be completely prevented with proper management and eventual removal. A concern involving the removal of lead-based paint is the safe disposal of lead-contaminated material. Solid

waste land disposal sites can be sources of groundwater contamination because of the generation of leachate caused by water percolating through the bodies of refuse and waste material. Those materials that do not degrade into innocuous substances (e.g., lead) are liable to accumulate somewhere in the biosphere and cause problems, especially in areas where the use of groundwater is of extreme importance (in arid climates, for instance).

In the United States, it has been estimated that at least 50 percent of the general population (and 95 percent of the rural population) rely on groundwater for their primary source of water (Jousma 1989). Experts have speculated that the use of groundwater will continue to increase at a rate of 25 percent per decade (Miller 1980). Groundwater offers a high quality, economical, and readily available source of drinking water. Improperly disposed of lead-contaminated waste can potentially damage this resource irreparably.

It is easy to dispose of waste with the belief that it will just disappear (i.e., "out of sight, out of mind"). However, while disposed items may not detrimentally impact the environment, the material or its components must move through ecosystems and will end up in definable situations where problems may arise. The single goal of waste disposal is to ensure the containment of potential environmental pollutants. To minimize the risk of groundwater contamination, the three main components of the waste disposal environment (the soil, the leachate, and the pollutant), which control the rate pollutants movement through soil, must be well understood (Fuller 1985). Currently, there are few guidelines and no standardized methods for estimating the movement of pollutants through soil. The slow development of better burial techniques has not been due as much to indifference by the communities or industries, as to the lack of knowledge of complex physical and biological systems (Fuller 1985), including:

1. Soil-waste reactions (chemical, physical, and biological) under both controlled and natural conditions
2. Migration reactions of specific pollutants (heavy metals, organic compounds, and organic solvents) through the complex-porous soil medium
3. Loading or concentration factors
4. The host of highly different potential pollutants in a single waste stream
5. The way one constituent affects another with respect to attenuation on retention in soils.

If the health and welfare of the American people is to be assured, more knowledge of the ultimate fate of lead in the landfill environment will need to be obtained. The

cost of improper disposal techniques is immense, both in terms of economy and human health.

### **Army**

The U.S. Army maintains 270 million square feet of family housing. Sixty-five percent of these structures (264,000 housing units) are more than 25 years old and are likely to have both interior and exterior surfaces painted with lead-based paint (Gooch 1993). The Army is dedicated to providing a healthful living and working environment for its employees, an objective that requires the control, and eventual removal and disposal of lead-based paint from residential and industrial structures. To date, there is no complete inventory of Army housing with lead-based paint, but the Army Policy Guidance states that the goal is "to inspect all facilities by 1994." Lead-contaminated structures will require remediation to meet current regulatory mandates and to ensure a safe living environment for Army personnel. Once lead is removed, the Army will be responsible for disposing of its abatement waste in an environmentally responsible manner.

The Safe Drinking Water Act gave the U.S. Environmental Protection Agency (USEPA) the authority to control the disposal of waste that may endanger underground water supplies. The USEPA has set the maximum concentration of lead in drinking water at 0.05 milligrams per liter to protect public health. Lead-based paint removed during abatement has the capability to contaminate groundwater with excessive levels of lead if improperly disposed. Proper site selection for the disposal of pollutants and the use of liners are the primary techniques currently available for minimizing the potential for groundwater contamination. A sound understanding of soil-solvent-lead interactions is essential to protection of groundwater supplies. Investigation of lead mobility in soil, and the variables that effect its leachability are needed to minimize future contamination of water supplies and the high expenses associated with remediation under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Currently, the majority of the waste generated by the Army is being disposed of at either municipal landfills or RCRA approved hazardous waste landfills. Improperly disposed of waste may cause additional expense to the U.S. Army under CERCLA legislation and may compromise human health. Without a complete knowledge of soil attenuation, biodegradation rates, transport rates, and stabilization mechanisms of pollutants, the full protection of the food chain and groundwater is not possible (Fuller 1985). Because of the potential magnitude of lead-contaminated waste that the Army may need to dispose of, a sound understanding of lead's fate in

the landfill environment is required to make environmentally sound disposal decisions.

## **Objective**

The objective of this study was to evaluate parameters that effect the movement of lead through soil using batch tests.

## **Approach**

1. A broad literature search was conducted into the historical and current use of lead; a more focused investigation reviewed the current status of research on the mobility of lead through soil.
2. Laboratory research was done to evaluate the effect of fulvic acid on the transport of lead through the subsurface using batch tests.
3. Laboratory results were analyzed, conclusions drawn, and recommendations made for further research.

## **Mode of Technology Transfer**

This research will form the basis for the Lead-Based Paint (LBP) Abatement Waste Disposal Guidelines currently being written.

## 2 Lead Use and Current Status

### Physical and Chemical Properties

Lead is a soft, bluish or silver-gray metal that is relatively inert. Its chemical symbol Pb derives from its Latin name "plumbum." Lead is unique among the toxic heavy metals in that it is relatively abundant in the earth's crust (Cheremisinoff 1993). Mineralogists have identified over 200 lead minerals, but only three are significant: galena (PbS), cerussite (PbCO<sub>3</sub>), and anglesite (PbSO<sub>4</sub>). Of these, galena is used for the commercial extraction of lead (Fergusson 1990). Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits that are genetically related to siliceous igneous intrusive rocks, but lead ore may occur in a variety of igneous, metamorphic, and sedimentary host rocks (Lovering 1976). Four short-lived radioactive isotopes <sup>210</sup>Pb, <sup>211</sup>Pb, <sup>212</sup>Pb and <sup>214</sup>Pb occur in nature as decay products of uranium and thorium. Table 1 lists the physical and chemical properties of elemental lead.

**Table 1. Physical and chemical properties of lead.**

Property*	Value
Atomic weight	207.22
Atomic number	82
Stable isotopes	204 205 207 208
Melting point (Celsius)	327.5
Boiling point (Celsius)	1750
Density g/cc	11.34
Ionization potentials	7.38 14.96
* Cheremisinoff 1993	

Lead has two oxidation states Pb(II) and Pb(IV) as well as the elemental state Pb(0). The tetravalent state is a powerful oxidizing agent, and the divalent state has a more stable oxidation level as seen from the following standard reduction potentials:

$$E^{\circ}(\text{Pb}^{4+}/\text{Pb}^{2+}) = 1.7\text{V}, \text{ and } E^{\circ}(\text{Pb}^{2+}/\text{Pb}) = -0.126\text{ V}$$

Natural inorganic forms of lead are primarily divalent, whereas the organic forms are tetravalent. Elemental lead is able to form complexes with soluble charged or electrically neutral organic or inorganic materials called ligands. With the exception of nitrate, chlorate, and chloride, the salts of lead are poorly soluble in water (WHO 1989). The solubility of relatively insoluble lead compounds can be increased by complex formation, such as chloro- or hydroxo- complexes and reactions with organic ligands (Fergusson 1990). Because of the multitude of reactions occurring in the natural environment, equilibrium models are limited in their ability to predict the

movement of lead through soil. In the absence of other ligands, the ionic species below pH 7.0 is  $\text{Pb}^{2+}$ ; under alkaline oxidizing conditions, the stable form is  $\text{PbO}_2(\text{s})$ . In the presence of dissolved  $\text{CO}_2$ , lead carbonate precipitates (Faust 1981).

## Lead Use in Society

Lead is the most widely used heavy metal in society. It has a number of properties, such as corrosion resistance, sound absorption, radioactive radiation absorption, anti-friction, and a low melting point that make it a useful metal. Lead has been used for the past 5000 years for a variety of purposes. The extensive use of lead in early human history can be attributed to its common occurrence in nature and ease of smelting. During the Iron Age (1200 to 500 BC), lead production was approximately 12,500 tons/year. The use of lead in ancient times peaked during the Roman period (500 BC to 500 AD) at around 27,000 tons/year. During this period of time, lead was used for water pipes, writing tables, coins and cooking utensils. The Romans also added lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) to wine to enhance its flavor. Not until the seventeenth century, was lead outlawed as a wine additive in France (Gooch 1993). After the fall of the Roman Empire (500 to 1000 AD), consumption dropped to 8,500 tons/year (Fergusson 1990). Today, world production exceeds 3.5 million tons/year, a far larger quantity than the production of any other toxic metal (Cheremisinoff 1993). Table 2 lists the common uses for lead in today's industrial society.

Because of the prevalent use of lead in early human history, physicians became aware of the health risks associated with its use. The Greeks and Romans used lead in many products, and were aware that, when workers were exposed to lead for extended periods of time, they would develop convulsions and often die. Chemical analyses of the bones of ancient Romans show high lead concentrations, in some cases 200 times that of modern levels. Historians attribute the madness of some Roman leaders to lead toxicity. The first clinical accounting of lead poisoning appeared in the first century BC. In France during the 1830s, painters and pigment manufacturers became aware of health problems associated with the use of lead; the manufacture of "white lead" was banned in Europe in the mid-1800s.

The problems associated with lead were not limited to only the Old World; in 1786, Benjamin Franklin cited his own "lead colic" from exposure to lead during typesetting. In today's society, it

**Table 2. Uses of lead.**

Use*	Percent
Lead batteries	60
Petrol additive	4
Rolled and extruded products	9
Pigments	13
Alloys	5
Cable sheathing	6
Ammunition	3
Total	100

\* Fergusson 1990



has been estimated that over 1 billion individuals worldwide have been poisoned by lead ( $>20$  mg/dL of blood) (Fergusson 1990). The general population is exposed to lead through air, drinking water, and food. The average daily intake of lead in the United States was 0.33 mg during the 1970s (Faust 1981). It is speculated that the average daily dose has decreased with the removal of lead from gasoline. However, some individuals may be exposed to higher doses through such specific sources as paint, occupational hazards, and recreation.

## Lead Use in Paint

Lead paints have good covering and anticorrosive properties and are relatively inexpensive. Some lead compounds used as pigments are red lead ( $\text{Pb}_3\text{O}_4$ ) and white lead ( $2\text{PbCO}_3 \bullet \text{Pb}(\text{OH})_2$ ), which are used in rust resistant paint;  $\text{PbCrO}_4$ , a yellow pigment used in road markings;  $\text{Ca}_2\text{PbO}_4$  (calcium orthoplumbate),  $\text{PbMoO}_4$  (lead molybdate), and  $\text{PbO}$  (massicot [lead monoxide]), which are used for painting galvanized iron. Not all lead in paint is used for pigmentation. Lead is also used as a drier in paint and primer. According to the USEPA, it is estimated that lead-based paint was applied to approximately two-thirds of the houses built in the United States prior to 1940, one-third of the houses from 1940 to 1960, and an unknown (but smaller) portion of U.S. homes built since 1960 (Cheremisinoff 1993). At the turn of the century, lead-paint was hailed as "the best paint money could buy." White-lead paint went on smoothly and protected wood structures from wind, rain, blistering sun and premature wood rot. For steel, red-lead was considered the first choice in rust prevention. "The fact that it is used to protect practically all structural iron and steel work, from the tallest skyscraper skeletons to the smallest railway bridges, is sufficient testimony to prove its worth" (Harn 1917). Table 3 lists ingredients for white paint obtained from a 1917 book published by the National Lead Company.

The health risks associated with the use of lead in paint have been known since the 1800s. However, it was believed that the benefits of using lead in paint outweighed the health risks. Residential use of lead-based paint was prohibited in 1978 and industrial use of lead-based paint has been decreasing for the past 3 to 4 decades because of more stringent regulations and the development of coating with better chemical resistance including vinyls, epoxies, urethanes, and zinc-riches (Trimber 1993). However even today, government and industrial institutions continue to use lead-based paint and primers (Gooch 1993). A 1991 Steel Structures Paint Council survey estimated that 38 percent of the steel in industrial facilities are coated with lead-based paint.

Table 3. Paint ingredient list from 1917.

Ingredients	Priming Coat	Second Coat	Third Coat
<i>New, Unpainted Wood Outside</i>			
Dutch Boy white-lead	100 lb	100 lb	100 lb
Pure raw linseed oil	4 gal	1.5 gal	3.5–4.5 gal
Pure turpentine	2 gal	1.5 gal	1 pint
Drier free from rosin	1 pint	1 pint	1 pint
How much paint it makes	9 gal	6 gal	6.5–7.5 gal
Coverage	5,175 sq ft	3,600 sq ft	3,900–4,500 sq ft
<i>For Repainting Old Wood Outside</i>			
Dutch Boy white-lead	100 lb	100 lb	
Pure raw linseed oil	2 gal	3.5–4.5 gal	
Pure turpentine	2 gal	1 pint	
Drier free from rosin	1 pint	1 pint	
How much paint it makes	7 gal	6.5–7.5 gal	
Coverage	4,200 sq ft	3,900–4,500 sq ft	

The large scope of the lead-based paint problem, combined with increasing public health concern about the effects of low-level lead exposure to young children, indicates the potential for a major nationwide abatement effort in the next 10 years. The 1988 Agency for Toxic Substances and Disease Registry reported to Congress that there were 5 million tons of lead contained in household paint in the United States. Many lead-based paint abatements, especially those involving removal and replacement of doors, windows, and trim painted with lead-based paint, produce large quantities of solid waste containing lead in varying concentrations (USAEHA 1993). The USEPA regulates the disposal of lead-based paint under RCRA legislation. The solid waste created during abatement is either classified as hazardous or nonhazardous based on leachability characteristics of the toxic metals found in paint. Elements present in paint such as barium, cadmium, chromium, and mercury in addition to lead can cause paint debris to be classified as hazardous; Table 4 lists leachable levels of these elements.

Paint debris classified as hazardous is subject to the RCRA Subtitle C rules and the USEPA hazardous waste number assignments. Hazardous materials commonly generated during abatement of lead-based paint include: paint chips, substrate, HEPA vacuum debris, dust from air filters, sludge from stripping, unfiltered liquid waste, blasting media, rags, sponges, mops, HEPA filters, air monitoring cartridges, scrapers, plastic sheeting, structural components, and other materials used for testing, abatement, and clean-up.

Table 4. RCRA definition of hazardous concentrations of toxic metals found in paints (based on leachability).

Element*	Concentration mg/L (ppm)
D005 Barium	100.0
D006 Cadmium	1.0
D007 Chromium	5.0
D008 Lead	5.0
D009 Mercury	0.2
* Trimmer 1993	

The high cost and liability associated with disposing of hazardous waste has provided an incentive to develop new disposal technologies and alternatives. Currently, several "new" methods are being used to dispose of lead paint removed from structures. Lead-based paint debris may be recycled, reclaimed, or stabilized and landfilled. The economic and environmental consequences of each alternative have not been thoroughly investigated and more research is needed to determine the costs and benefits of each option.

## Lead in the Environment

Geotechnical data indicates that, in the United States, the concentrations of lead in most surface materials range from 10 to 30 ppm (Cheremisinoff 1993). Much higher concentrations of lead have been observed as a result of mining and smelting activities, disposal of sewage sludge and other wastes, and combustion emissions (Carter 1993). During the 1970s, urban soil contamination by lead was primarily the result of lead-based paint weathering, except in the immediate vicinity of trafficways where contamination was due to the use of leaded gasoline (Griffin 1975). Lead-based paint on old residential structures and industrial facilities continues to contaminate soil and pose a significant health hazard. The accumulation of lead at the soil surface is of concern because children consume dust and dirt during normal hand-to-mouth activity, resulting in elevated blood lead levels (Carter 1993). Lead-based paint and lead-contaminated dust and soil are the primary sources and pathways for childhood lead exposure (Gooch 1993). In 1985, the Centers for Disease Control reported that "lead in soil and dust appears to be responsible for blood lead levels in children increasing above background levels when the concentration in the soil or dust exceeds 500 to 1000 ppm" (Trimber 1993). The USEPA has unofficially adopted an action level of 500 ppm in soil (Gooch 1993).

The tendency of lead to be relatively immobile in soil results in an extreme vertical-concentration gradient when it is from an external source. High concentrations of lead are still found in top soils that were contaminated in the 4th century B.C. (Fergusson 1990). Plants play an important role in maintaining the high surface concentration of lead. During growth, plants may take up lead and store it in their tissue. The amount of lead that is assimilated depends on the soil and vegetation involved. Studies have shown the importance of soil type, cationic exchange capacity, carbon content, and crop type on the lead concentration in plants. Soil scientists have found that a soil with a high exchange capacity is much less likely to release lead to plants than a soil with a low exchange capacity. When the plant decays, the lead remains behind at the surface where it is complexed with organic material. In the case where the soil surface is covered with forest litter, lead

contamination may not reach the soil surface at all, but rather is retained by the organic horizons (Boggess 1976). The natural mechanisms of building up organic matter in soil along with lead's relative immobility, result in concentrations highest at the ground surface (Griffin 1975).

Natural lead deposits do not normally move appreciably in typical ground or surface water. Any lead dissolved from primary sulfide ore tends to combine with carbonate or sulfate ions to form insoluble lead carbonate or lead sulfate, or to become adsorbed by ferric hydroxide. However, it has been observed that the concentration of lead from natural sources has prevented the use of some groundwater sources for domestic or irrigation purposes (Fuller 1978). Mechanical disintegration and transportation of these insoluble lead compounds can remove lead from the surface of lead ore bodies and disperse it to some extent. Lead can also be leached by acidic waters, particularly those that are rich in organic material, and travel in solution as soluble lead organic complexes (Lovering 1976). A study performed in the 1960s of groundwaters in the United States and Puerto Rico revealed that 80 percent of the samples contained less than 10 µg/L of lead. Lead has a low solubility in water that contains moderate concentrations of bicarbonate ions and has a pH near 8. Many groundwaters display these properties, and thus are expected to be low in dissolved lead concentrations.

Natural concentrations of lead in fresh water have been estimated to be about 0.5 mg of Pb/L. The most significant source of lead in natural surface waters is from the atmosphere (Faust 1981). Runoff waters may also have elevated lead levels (40 to several hundred mg/L) if the pH and alkalinity are low (Faust 1981). Available lead measurements suggest that little of the total lead is in solution in hard water. Lead salts are poorly soluble in water, and the presence of other salts reduces the availability of lead to organisms because of precipitation (WHO 1989). However, it has been found that highly saline waters contain appreciably higher concentration of lead than fresh water (Lovering 1976). Natural waters are one the primary sources of lead exposure to humans. The majority of lead found in drinking water can be attributed to lead pipes and solder. Although drinking water typically has a low concentration of lead, the daily dose is magnified because of the large amount consumed by humans. The Environmental Protection Agency estimates that the average drinking water comprises 20 percent of the total exposure to lead (Cheremisinoff 1993).

The natural background concentration of lead in the atmosphere has been estimated to be approximately 0.0006 mg Pb/m<sup>3</sup> of air. Until recently, 98 percent of the total lead discharged to the atmosphere came from the combustion of leaded gasoline (Faust 1981). In November 1991, the USEPA Hazardous Waste Treatment Council

listed the combustion of used motor oil as the primary source of airborne lead (Gooch 1993). Other sources of atmospheric lead resulting from human activity are combustion of fossil fuels, weathering paint, and smelting of lead ores. The residence time of lead in the atmosphere is estimated to range from 7 to 30 days (Faust 1981). With the exception of volcanoes and forest fires, natural sources are associated with lower temperature emissions that contain larger particles that tend to settle out more rapidly (Hutchinson 1987). Based on a review of epidemiological studies, the USEPA selected a ratio of 1.0 to 2.0 for estimating the impact of air lead levels on blood lead levels in children; that is, USEPA assumed that each mg Pb/m<sup>3</sup> in the air contributes 2 mg Pb/100 mL to the blood lead level (Cheremisinoff 1993).

Ice cores are commonly used to measure the global impact of a pollutant over time. Ice cores obtained from the North Pole show that the lead concentrations in the most recent ice layers are 10- to 100- fold higher than the values in prehistoric times. Furthermore, these recent values are about 10 times greater than those of similar age at the South Pole. This is due to greater industrialization in the northern hemisphere compared to the southern hemisphere. Most lead remains in the northern hemisphere due to meteorological phenomena, causing a rise in lead concentrations in Greenland, while no comparable rise occurs in the Antarctic (Boggess 1976). However, even at the South Pole, the present-day rate of lead deposition is 2-5 times higher than in pre-technical times (Hutchinson 1987). It is obvious that the use of lead in society has had an observable impact on the environment.

## Lead's Impact on Human Health

It is well established that lead is toxic to humans at high doses, and that levels of exposure encountered by a fraction of the population are high enough to constitute a health hazard (Cheremisinoff, 1993). Lead is naturally absorbed into the body by inhalation and ingestion on a daily basis, but is not considered an essential element to human nutrition. It is a cumulative poison that tends to be preferentially deposited in calcified tissues, but is also found in the brain, liver, kidney, aorta, and muscles (Faust 1981). The half-life of lead in bone exceeds 20 years (Gooch 1993). Lead deposited in women's bones can be mobilized during pregnancy, when it can affect the unborn fetus. Although lead is not as dangerous as some other heavy metals, it is considered more dangerous as a general population toxin because of its wide use in society and elevated concentration in the environment. Despite significant reductions in the use of lead over the past few decades, lead poisoning remains among the top 10 epidemics in the United States (Cheremisinoff 1993).

Lead absorbed from the environment affects humans in various ways. However, there is no evidence available that lead has carcinogenic or teratogenic effects on humans (Fergusson 1990). Lead in the human body disrupts energy metabolism, interferes with neural cell functions, disrupts the formation of heme, inhibits communication, and decreases the nerve conduction velocity (Gooch 1993). The most common symptom resulting from lead exposure is the inhibition of enzyme formation. Lead biochemically reacts with the sulfhydryl group in proteins. The reaction inhibits the enzyme responsible for catalytic biosynthesis of heme. This results in an impairment of hemoglobin, causing oxygen starvation and finally anemia. This biochemical activity has been confirmed to be responsible for increased hyperactive and delinquent behavior among children, adults, and animals due to a direct relationship between the activities of blood and brain enzymes (Cheremisinoff 1993). Table 5 lists many of the acute and chronic health problems associated with the intake of lead.

In the 1920s, childhood lead poisoning was recognized as a common and often fatal childhood disease. The Centers for Disease Control established a maximum blood lead level concentration of 25 micrograms of lead per deciliter of blood in children in an effort to decrease the number of childhood lead poisoning cases. However, levels as low as 10 to 15 mg/dL have been found to cause serious health effects. Childhood lead poisoning is still one of the most common pediatric health problems in the United States (Gooch 1993). It is anticipated that the acceptable blood lead level will be lowered to 10 mg/dL for children in the near future. For adults,

**Table 5. Lead-associated health problems.**

<b>Acute (Short-Term)*</b>	<b>Chronic (Long-Term)</b>
Tend to be nonspecific	Some effects may be reversible such as high blood pressure, but can cause permanent damage to:
<ul style="list-style-type: none"> <li>• irritability</li> <li>• fatigue</li> <li>• depression</li> <li>• headaches</li> <li>• loss of appetite</li> <li>• hard to concentrate</li> <li>• sleep problems</li> <li>• pains in muscles and joints</li> <li>• stomach cramps (colic)</li> <li>• reproductive problems</li> </ul>	<ul style="list-style-type: none"> <li>• nerves of hands and feet</li> <li>• brain</li> <li>• kidneys</li> <li>• reproductive system</li> </ul>
<b>Men</b>	<b>Woman</b>
<ul style="list-style-type: none"> <li>• decreased sex drive</li> <li>• problems having an erection</li> <li>• decreased fertility</li> <li>• birth defects and miscarriage in partners</li> </ul>	<ul style="list-style-type: none"> <li>• decreased fertility</li> <li>• miscarriages</li> <li>• premature births</li> <li>• stillbirths</li> <li>• learning and behavioral problems in offspring</li> </ul>
* Cheremisinoff 1993	

abatement workers, and women of child-bearing age, blood lead levels in excess of 30 mg/dL are of serious health concern (Cheremisinoff 1993). Even at the blood lead levels specified as "safe," some damage occurs to the human body (Table 6).

## Analysis Techniques

Two analytical techniques are specified in legislation (by the USEPA) for determining the leachability potential of solid waste at land disposal sites. The methods simulate landfill conditions that could result in a release of soluble pollutants into the soil. If toxic pollutants (such as lead) enter into an aquifer that is used for drinking water, the public's health may be at risk. The purpose of the two tests (TCLP and EP-Tox) is to assess the potential for pollutant movement, so that the waste may be disposed appropriately. Both techniques use standard laboratory procedures discussed below to determine the concentration of lead released.

The Toxicity Characteristic Leaching Procedure (TCLP) measures levels of both volatile and semi-volatile organics, as well as heavy metals such as lead. The objective of the TCLP test is to measure the "worst case leachate concentrations" in the field. Under the land disposal restrictions program, lead must register a level of less than 5 ppm on a TCLP test to be eligible for land disposal. This level is 100 times greater than the National Interim Primary Drinking Water Standard for lead. The Extraction Procedure Toxicity Test (EP-Tox) has traditionally been used most often to characterize hazardous waste. Prior to March 1990, the EP-Tox was used to determine whether a waste was hazardous under RCRA. The March 1990 revision of the RCRA Toxicity Characteristic replaced the EP-Tox with the TCLP

**Table 6. Effects of lead at different blood lead levels.**

Blood Lead Level (mg/dL)*	Effect
4-6	Inhibits enzyme d-aminolevulinic acid dehydrase
15	Elevation of erythrocyte protoporphyrin in blood
20-25	Chromosomal abnormalities
30	Toxicity to fetus
30-40	Reduce fertility in women
30-40	Altered spermatogenesis for men
40	Reduced peripheral nerve conduction
40	Reduced hemoglobin synthesis
40-60	Psychological sensory and behavior changes
50	Impaired kidney function
>50	Anemia
50-60	Peripheral neuropathy
100-120	Encephalopathy

\* Fergusson 1990.

test. However, lead is an exception; either method can be used even though the TCLP is considered to be more reliable test than the EP-Tox. The EP-Tox does not include analysis of volatile organics, but otherwise will tend to agree with the TCLP test results (Cheremisinoff 1993). Correspondence between the two tests is commonly observed because they use a similar method. For example, both tests use acetic acid as a leaching solvent. The TCLP is also easier to conduct in the laboratory and is less prone to technician error than is EP-Tox (Trimber 1993). Procedures for conducting the EP-Tox and TCLP are found in Appendix II of 40 CFR 261. Other leachability potential tests are used to simulate various conditions, but the most widely recognized are the tests mentioned above.

The concentration of metals in environmental samples can be determined using a variety of analytical procedures, such as atomic absorption, atomic emission inductively coupled plasma spectroscopy, ion chromatography, and colorimetric procedures. Each test has different detection limits, expenses, and technician training and time requirements. Investigation of each analytical method is required to determine which is best suited for a particular application. The techniques most commonly used for paint are briefly reviewed below.

Atomic absorption (AA) has rapidly become the most widely used analytical technique for quantitative trace metal analysis. The technique is directly applicable to 68 elements. Atomic absorption is essentially a solution-based technique with very limited applications for the analysis of solids or gases. Advantages include specificity, speed, ease of use, and a high degree of sensitivity. Detection limits are typically in the sub-ppb to low ppm range by weight in the sample solution. A graphite furnace AA system provides a 50- to 500-fold improvement in sensitivity relative to flame AA. While various interferences exist, they are usually moderate in nature with documented methods of control. Procedures for analyzing lead are found in ASTM D-3335 and in USEPA Manual SW-848, Methods 7000 and 7421.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) can analyze multiple elements simultaneously. This method is approximately 10,000 times more sensitive than AA. The primary disadvantages of using this method are the high equipment and maintenance costs. Procedures for analyzing lead are found in USEPA Manual SW-848, Method 6010. Colorimetric procedures for determining the presence of lead in paint samples include the Rhodizonate and Sodium Sulfide Spot Tests. These two qualitative tests are used to determine if further testing (TCLP) is required before disposal.



## Legislation

In the past 2 decades, federal regulations have successfully reduced blood lead levels in the entire U.S. population. Between 1976 and 1980, the national mean blood lead levels declined 37 percent due to the decreased use of leaded gasoline (Gooch 1993). Six federal agencies (Table 7), acting under authority of at least eight separate laws, have developed regulations and administration programs intended to protect the public health from lead hazards (Cheremisinoff 1993).

**Table 7. Regulatory agencies.**

- |  |
|--|
| <ul style="list-style-type: none"> <li>• Agency for Toxic Substances and Disease Registry</li> <li>• Centers for Disease Control</li> <li>• Consumer Product Safety Commission</li> <li>• Environmental Protection Agency</li> <li>• Department of Housing and Urban Development</li> <li>• The Occupational Safety and Health Administration</li> </ul> |
|--|

Because contamination of groundwater has occurred in every state and is being detected with increasing frequency, regulatory agencies and courts have been developing guidelines, laws, and rules to protect this resource. Many of these laws address disposal issues affecting the landfilling of lead-contaminated materials.

Congress passed the first lead paint poisoning legislation in 1971 to reduce the alarmingly high incidence of lead poisoning and elevated blood lead levels among inner-city children. The Consumer Product Safety Commission began to regulate the use of lead in manufactured paint in 1973. The Commission established a maximum lead content in paint at 0.5 percent by weight in the dry film of a paint sample under the Federal Hazardous Substances Act. The commission chose to use the National Consumer Information and Health Promotion Act of 1976 to impose more stringent controls on the lead in paint. The Act defines lead-based paint as any paint that contains more than 0.06 percent, 600 ppm, lead by weight in the nonvolatile content of the paint or the equivalent measure of lead in the dried film already applied. In 1992, the Residential Lead-Based Paint Act, commonly referred to as Title X, established the elimination of lead-based paint hazard from housing as a national goal. Title X, which amends the Toxic Substances and Control Act, provides a timeline to accomplish the goal. Currently, there is no definition for industrial lead-based paint or regulations for control at industrial facilities, although the levels of lead in traditional industrial paints have been as high as 30 percent (Trimber 1993).

The Lead-Based Paint Poisoning Prevention Act, as amended, provides the Department of Housing and Urban Development with regulatory and research responsibilities for eliminating the hazards of lead-based paint poisoning in HUD-associated and other specified housing. The Act requires abatement when lead is present at or above an "action level" of 1.0 mg/cm<sup>2</sup> or 0.5 percent by weight. The objective is to

eliminate childhood lead poisoning caused by the ingestion of lead paint in residential structures. The current law also authorizes the U.S. Department of Health, Education, and Welfare through the Center of Disease Control to underwrite the cost of detection and treatment programs. Their primary mission is to prevent undue lead absorption and lead paint poisoning through screening, diagnosis, treatment, and follow-up of children in high-risk areas.

The Consumer Product Safety Act of 1977 provides general authority to the Consumer Product Safety Commission to ban as hazardous any consumer product that presents an unreasonable risk of injury. Under this authority, the commission has banned from sale in interstate commerce paint and surface coatings, and toys and furniture with painted surfaces containing more than 0.06 percent lead. These controls became effective in February 1978. Regulations relating to the Act are found in 16 CFR 1303.

Occupational exposure to lead is controlled by OSHA. The Occupational Safety and Health Act of 1970 was passed by Congress to assure safe and healthful working conditions for working men and women. The OSHA Lead Standard established two air exposure limits, both applicable over an 8-hour, time-weighted average, an action level of 30 mg/m<sup>3</sup> of air and a permissible exposure limit of 50 mg/m<sup>3</sup> of air. OSHA uses blood lead levels (PbB) to assess occupational exposure to lead. PbB measurements indicate the amount of lead in the blood stream, not in tissues. This technique reflects only recent exposure to lead, not the lifelong dose. Prevention of adverse health effects for most workers, from exposure to lead throughout a working lifetime, requires that workers blood lead (PbB) levels be maintained at or below 40 mg/100g. PbB levels should be kept at or below 30 mg/100g to minimize adverse reproductive health effects to the parents and to the developing fetus. OSHA also feels that the blood lead level in children should be maintained below 30 mg/100g with a population mean of 15 mg/100g. The lead standard can be found in 29 CFR 1910.1025.

The concentration of contaminants that can be found in potable water is defined by the Safe Drinking Water Act (SDWA). The term "contaminant" is defined in the SDWA as any physical, chemical, biological, or radiological substance or matter in water. The SDWA was passed by Congress in 1974 to respond to accumulating evidence during the 1970s about the health threat posed by unsafe levels of contaminants in public drinking water supplies. The Act was designed to achieve uniform safety and quality of drinking water by identifying contaminants and establishing maximum acceptable levels for the pollutants. Since about one-half of the nation's drinking water is drawn from underground sources, the Act has obvious application to groundwater quality.

Lead in drinking water has been regulated by the U.S. Health Department for decades. The Lead Rule, published on 18 August 1991 in the Federal Register (53 CFR 31516), addresses lead levels in source water as well as entry of lead into water from corrosion of distribution piping and household plumbing materials. The amended National Primary Drinking Water regulation of 1991 has set the maximum contaminant level goal (MCLG) for lead at zero and the action level at 15 mg/L (ppb). The current maximum contaminant level (MCL) for lead is 50 mg/L. In 1986, Congress banned the use of lead solder containing greater than 0.2 percent lead and restricted the lead content of faucets, pipes, and other plumbing materials to 8.0 percent.

The Clean Water Act is a federal pollution control law that applies to both ground and surface waters because they are hydrologically connected. Funding was provided to states for water quality management planning and implementation, which includes groundwater. Lead-contaminated materials discharged into waters of the United States require a National Pollution Discharge Elimination System Permit to remain compliant with the Act. The Clean Water Act is addressed in 40 CFR Subchapter D, Parts 100 through 149.

The Clean Air Act, as amended, requires the administrator of the U.S. Environmental Protection Agency to promulgate national primary (health) and secondary (welfare) ambient air quality standards for air pollutants that endanger public health and welfare. On 5 October 1978, in accordance with these provisions, the USEPA promulgated a primary ambient air quality standard of 1.5 mg Pb/m<sup>3</sup>. This standard addresses the problem of human exposure to lead emitted into the atmosphere from various stationary and mobile sources. This Act has indirectly increased the volume of solid waste being disposed of at landfills because of restrictions on incineration. The Clean Air Act is addressed in 40 CFR Subchapter C "Air Programs," encompassing Parts 50 through 99.

RCRA was enacted in 1976 after threats to human health and the environment posed by toxic and hazardous wastes had become matters of real public concern. The specific impetus for RCRA's passage was Congressional concern for the special dangers caused by unsound waste disposal practices, mainly in landfills and open generation, transportation, treatment, storage, and disposal. Under RCRA's "cradle-to-grave" philosophy of waste management, the generator retains responsibility for the waste indefinitely. Waste is declared hazardous if it fails any of the following tests: ignitability, corrosivity, reactivity, or extraction procedure as defined in 40 CFR 261, or if listed as hazardous by the USEPA. The USEPA hazardous waste number assigned to lead is D008. A generator of waste may rely on the results of prior testing, experience, knowledge of the waste, or process generating the waste

in evaluating whether their waste is hazardous (USEPA 1993). This option does not release the generator from any liability because the generator is ultimately responsible under Environmental Protection Agency regulations for the proper characterization and disposal of their waste. The federal RCRA regulations are found in 40 CFR 240 through 280. However, most states administer the RCRA program for the USEPA, and the state program may be more strict than the federal.

Land Disposal Restrictions found in 40 CFR 268 require that lead-contaminated waste be treated before land disposal in a hazardous waste landfill. These restrictions were imposed primarily to protect groundwater. The specific restrictions associated with lead and other hazardous pigments used in paints such as barium, cadmium, and chromium are found in 40 CFR 268.35. The treatment methods identified for this type of waste include microencapsulation and stabilization. A common treatment technology involves grinding and mixing the refuse into a cement slurry (USAEHA 1993). The USEPA's Ground Water Protection Strategy is planning to use RCRA's authority to prevent the siting of disposal sites above Class I aquifers (irreplaceable sources of drinking water, ecologically vital or highly vulnerable to contamination) (Barcelona 1990). RCRA has the authority to manage hazardous waste, but does not address the clean-up of existing sites containing hazardous waste, nor does it address the release or spills of hazardous substances. These problems are covered under CERCLA regulations.

CERCLA was enacted in 1980 in response to the notorious Love Canal incident, which focused Congressional attention on the serious and widespread health threats posed by abandoned hazardous waste disposal sites. Congress established Superfund to enable the federal government to undertake prompt cleanup of especially dangerous sites, and later to seek reimbursement from responsible parties. CERCLA applies cleanup, funding, and liability provisions as triggered by a release or threat of release of a hazardous substance from a facility. CERCLA defines a hazardous material as any substance designated by the Clean Air Act, Solid Waste Disposal Act, Clean Air Act, or Toxic Substances Control Act as being hazardous. Lead is considered a hazardous waste under RCRA, and is regulated under both the Clean Air and Clean Water Acts. A release of materials containing 1 lb of lead, with a mean diameter of less than 0.1 mm in less than 24 hours, can trigger a CERCLA response. The CERCLA requirements are found in 40 CFR Subchapter J, Parts 300 through 373.

### 3 Leachate

#### Environmental Concerns

Burial of wastes, under controlled conditions, has yet to reach the state where there is absolute assurance of complete environmental protection (Fuller 1985). Groundwater pollution caused by leachate is the major environmental concern at landfills. Originally, landfills were designed to reduce air pollution and unsightly trash that accompanied open dumping and burning. They soon became the disposal method for every conceivable type of waste. Many landfills, particularly older ones, are poorly designed and leach contaminants into groundwater sources (Bedient 1994). Leachate is formed primarily by the percolation of rainwater through an open landfill or the cap of a closed one.

A secondary source of water is the initial moisture content of the waste (Harris 1988). When the field capacity of a soil is reached, leachate begins to form and move through the subsurface. Contamination due to the organic fraction is the primary concern at typical landfills with migration of heavy metals being a secondary concern. Consumption of groundwater contaminated with organics in most circumstances poses little hazard to health because people and animals find the water unpalatable. In some situations however, organics at concentrations that are not considered safe will have no taste or odor. Water contaminated by trace metals generally present a more serious problem because they are palatable, not biodegradable, and not easily detected (Jousma 1989).

Preventative measures are required to protect aquifers from contamination because subsurface transport is slow; the consequences of improperly designed landfills may not emerge for decades (Christensen 1989). Once contamination has occurred, costly long-term remediation may be required or the groundwater may be so extensively contaminated that existing remedial techniques may be ineffective. The consequences of improper disposal techniques have already been realized at some landfills. Today, they are Superfund sites.

## Typical composition

Leachate quality is influenced by biological, chemical, and physical processes that occur in a landfill. In most cases, leachate is heavily polluted, containing several grams of dissolved matter per liter. Table 8 lists the composition of a typical leachate.

Reduction and oxidation processes control the distribution of species such as  $O_2$ ,  $Fe^{2+}$ ,  $H_2S$ ,  $CH_4$  and the mobility of heavy metals (Appelo 1993). The soil-liquid interface of most organic-containing leachates is anaerobic. The mobility of heavy metals is typically greater under anaerobic soil conditions (Fuller 1977). It is generally observed in natural environments that redox processes proceed from the highest energy downward. Oxygenated water that infiltrates into a landfill that contains materials rich in organic matter will first be freed of oxygen and then nitrate. Sulfate is reduced after the nitrate is consumed and then methane may appear in the water (Appelo 1993).

The composition of a leachate determines which and to what extent particular constituents migrate through the subsurface. For example, the addition of a reductant, like downward leaching of dissolved organic matter from a landfill, can have an impact on the mobility of lead. The U.S. Army Environmental Hygiene Agency has identified lead concentrations exceeding the Safe Drinking Water Act's MCL of 0.05 mg/L in leachate from some construction/demolition debris landfills (USAEHA 1993). Under certain conditions, lead is solubilized as either a chloride or sulfate, both of which are slightly soluble in water and can readily

**Table 8. Range of leachate constituent concentrations.**

Parameter (mg/L, except where noted)*	Range
BOD	4 - 57,700
COD	31 - 89,520
TOC	0 - 28,500
Total volatile acids as acetic acid	70 - 27,700
BOD/COD (ratio)	0.02 - 0.87
COD/TOC (ratio)	0.4 - 4.8
Total Kjeldahl nitrogen (mg/L as N)	7 - 1,970
Nitrate nitrogen (as N)	0 - 51
Ammonia nitrogen (as N)	0 - 1,966
Total phosphates	0.2 - 130
Orthophosphates	0.2 - 120
Total alkalinity (as $CaCO_3$ )	0 - 20,850
Total hardness (as $CaCO_3$ )	0 - 22,800
Total solids	0 - 59,200
Total dissolved solids	584 - 44,900
Specific conductance (micro $\Omega$ /cm)	1,400 - 17,100
pH	3.7 - 8.8
Calcium	60 - 7,200
Magnesium	17 - 15,600
Sodium	0 - 7,700
Chloride	4.7 - 4,816
Sulfate	10 - 3,240
Chromium (total)	0.2 - 18
Cadmium	0.3 - 17
Copper	0.005 - 9.9
Lead	0.001 - 2.0
Nickel	0.2 - 79
Iron	4.0 - 2,820
Zinc	0.6 - 370
Methane gas (composition)	(up to 60%)
Carbon dioxide	(up to 40%)

\* Ray 1986.

leach through soil and into groundwater (Cheremisinoff 1993). It has been observed that, at high concentrations of organic carbon and low pH, higher concentrations of lead are mobilized (Christensen 1989). Therefore, the disposal of acid or acid-forming waste can release metals into solution (Fuller 1977). Leachate composition is an important parameter in determining the potential for the movement of lead at a disposal site.

## Age

Leachate is a chemically dynamic fluid continually changing over time. The changes have a dramatic effect on the movement of contaminants (Harris 1988). Pollution movement (including metals) is much more pronounced during the early stage of biodegradation and leachate generation (Fuller 1985). There are two general biological phases that occur in the life of a landfill, the acetogenic and the methanogenic phases. The acetogenic phase is characterized by high organics with BOD<sub>5</sub>/COD ratio > 0.4 and low pH, methane content, and gas production. The methanogenic phase is characterized by high methane content and pH, but the BOD<sub>5</sub>, COD, and BOD<sub>5</sub>/COD ratio are relatively low (Christensen, 1989).

The elevated BOD<sub>5</sub> to COD ratio during the acetogenic phase indicates an increased biodegradation of organic matter, which is not the case in the methanogenic phase. Young MSW leachates contain volatile acids as well as higher molecular weight acids. The large amounts of organic acids released in the acetogenic phase result in depressed pH values. The low pH values cause an increase in the solubility of inorganic substances (Christensen 1989). Freshly deposited waste will emit acidic leachate for approximately 18 months, after which the methanogenic phase will begin. During the acetogenic phase, the soil and soil liners will not retain heavy metals to the extent often observed during the methanogenic phase (Fuller 1985). Table 9 lists the changes in the leachate composition.

Following waste deposition, compaction, and placement of daily and (in due time) final cover materials, waste environments rapidly become anaerobic as oxygen is used by microbes. Dissolved oxygen and nitrate will first be removed with the production of large quantities of CO<sub>2</sub> that often give rise to carbonate dissolution and strongly enhanced alkalinity. Subsequently, Mn- and Fe-oxides in the sediments are reduced, releasing large amounts of ferrous iron and manganese (Appelo 1993). Studies have shown that, above a given threshold, metals exert a toxic effect on biostabilizing microorganisms (Christensen 1989). If a landfill experiences a high loading of lead or other heavy metals, decomposition of material may not occur (Chittaranjan 1986). Provided this does not take place, anaerobic bacteria then

become dominate and hydrolyze and ferment organic matter, degrading complex organic molecules to produce short-chain acids, ammonia, and carbon dioxide. During this stage, acidic conditions develop with the pH falling to about 5.5. If rainfall infiltration and leachate volumes are controlled, further degradation of organic acids occurs, ultimately resulting in the conversion of acetate to methane and carbon dioxide by methanogens. Hydrogen gas is also used by methanogens to convert carbon dioxide to methane and water. The pH is maintained at or near 7 during this final phase of refuse degradation, resulting in in-situ precipitation of heavy metals (Bradshaw 1992). Figure 1 shows the biological processes.

The following summarizes the leachate changes observed during the first 3 years of biodegradation. Fuller and Alesii (Fuller 1985) have reported the changes to be approximately:

1. pH rises from 3.5 to 7.0
2. Oxidation-reduction potential rises from a low of about 60 to 150 Eh
3. Sulfide rises several fold
4. Rate of sludge formation and accumulation rises greatly with time
5. Free volatile acids decrease from an original maximum, about tenfold
6. Soluble TOC decreases about 100-fold, BOD and COD roughly follow the trend of TOC
7. Electrical conductivity (EC) and soluble inorganic salts decrease several fold
8. Soluble heavy metal concentration decrease rapidly, sometimes completely disappearing from detection with time
9. Soluble Fe decreases as much as fivefold
10. Soluble P decreases several fold, sometimes disappearing from ready detection
11. Common soluble ions (Ca, Mg, Na, K, Cl, and SO<sub>4</sub> for example) decrease markedly with time, but do not disappear. They are always present though sometimes at relatively low levels. They accumulate on the particle solid surfaces as precipitates and sorbates where they can still be active in penetrating the site-enveloping soil.

**Table 9. Leachate characteristics, acetic and methanogenic phases.**

Parameter	Average	Range
<i>Acetogenic Phase</i>		
pH	6.1	4.5-7.5
BOD <sub>5</sub> (mg/L)	13,000	4,000-40,000
COD (mg/L)	22,000	6,000-60,000
BOD <sub>5</sub> /COD	0.58	
SO <sub>4</sub> (mg/L)	500	70-1750
Ca (mg/L)	1200	10-2500
Mg (mg/L)	470	50-1150
Fe (mg/L)	780	20-2100
Mn (mg/L)	25	0.3-65
Zn (mg/L)	5	0.1-120
Sr (mg/L)	7	0.5-15
<i>Methanogenic Phase</i>		
pH	8	7.5-9
BOD <sub>5</sub> (mg/L)	180	20-550
COD (mg/L)	3,000	500-4500
BOD <sub>5</sub> /COD	0.06	
SO <sub>4</sub> (mg/L)	80	10-420
Ca (mg/L)	60	20-600
Mg (mg/L)	180	40-350
Fe (mg/L)	15	3-280
Mn (mg/L)	0.7	0.03-45
Zn (mg/L)	0.6	0.03-4
Sr (mg/L)	1	0.3-7
* Christensen 1989.		



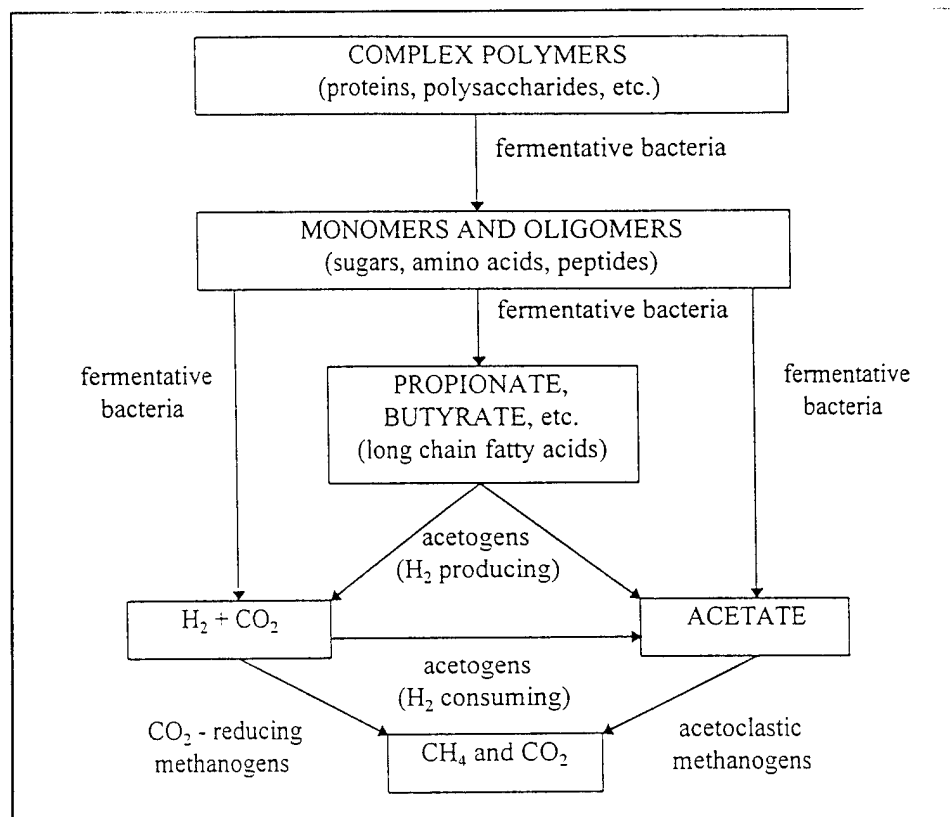


Figure 1. Anaerobic digestion of complex compounds.

## Leachate Control

Acceptable landfill sites that are close to metropolitan areas are becoming increasingly difficult to find. Because of the high costs of transporting solid waste, locations that were at one time considered geologically or hydrologically unacceptable are being reconsidered. Physical and chemical modifications to the sites are required to prevent environmental contamination. Leachate is the primary pathway for pollutants to enter the environment at a landfill. Regardless of the geologic or hydrologic conditions, preventative measures must be taken to inhibit the movement of leachate out of the disposal site. The current design philosophy for landfills is to use liners to minimize the hydraulic transport of contaminants (Bonaparte 1990).

The potential for leachate to migrate through the subsurface and cause extensive pollution requires that landfills install impermeable liners, leachate collection systems, and monitoring wells to remain in full compliance with 40 CFR, Part 268.52 (L)(2). Waste transformation and the use of amendments to liners can also help contain contaminants within a landfill site, reducing the risk of groundwater contamination and future liability for the waste generator.

Modern landfill design requires the collection and treatment of leachate. Many "new" disposal sites use local, publicly owned treatment works to treat collected leachate. The inability of municipal wastewater treatment plants to remove metals before disposal to receiving waters poses a significant risk to the biosphere (Chittaranjan 1986). There are two solutions to this problem: (1) on-site treatment, designed to remove the metals of concern, and (2) the use of site-appropriate loading rates along with natural attenuation to minimize the potential detrimental effects of metal migration.

Waste stabilization/solidification is used to reduce the quantity of toxic substances leached during the EP-Toxicity test and TCLP to nonhazardous levels. Solidification refers to a process in which materials are added to the waste to produce a solid. Stabilization refers to processes by which wastes are converted to more chemically stable forms. Stabilization reduces the mobility of lead while solidification reduces the access of water to the lead (Cheremisinoff 1993). Both organic and inorganic compounds are unitized to stabilize and solidify wastes. Typically waste is mixed with lime/fly ash mixtures, cement, concrete mixtures, or other formations. Water is then added and the mixture is allowed to form a solid mass. The solid form is easier to handle and less likely to expose the environment to toxic contaminants.

Amendments added to liners can help retard the movement of pollutants at disposal sites. The use of crushed limestone is one technique used to control the movement of heavy metals in landfills. The limestone raises the pH causing the precipitation and sorption of carbonate and calcium compounds. Addition of fly ash has a similar effect on the movement of metals in a landfill. An alternative to hydroxide precipitation is the addition of sulfides ( $\text{FeS}$  or  $\text{NaHS}$ ), which also precipitates metals (Harris, 1988). Organic waste such as bioresistant nut hulls may be used along with soil liners to further discourage migration of trace and heavy metals (Fuller 1985). The organic material complexes with heavy metals in the leachate, removing them from solution. The addition of phosphorous to the soil also markedly reduced the mobility of lead (Griffin 1975). These techniques should be used in conjunction with appropriate linear and leachate collection systems.

## 4 Soil

### Attenuation of Pollutants

Soils have a great capacity to retain contaminants, and serve as a depository for a large fraction of the pollutants generated worldwide. In recent times, there has been some concern about the abuse of this natural phenomenon to the extent that critical loads may be exceeded in some areas (Cresser 1993). Soil is a natural sink for lead, and over time, lead accumulates in soil from leaded gasoline emissions, metal refining and smelting, industrial emissions, and weathered lead-based paint (Gooch 1993). The rate and degree of attenuation are a function of the type of contaminant and of the local hydrogeologic framework. All soils are not equally effective in attenuating or retaining pollutants (Figure 2).

Therefore, before siting a landfill, the properties of the unsaturated and saturated zones must be investigated to determine the likelihood of a detectable impact on groundwater. Although many variables affect the attenuation of pollutants, the pollution risk of existing and future disposal sites may be estimated.

Physical soil characteristics that affect the movement of pollutants (such as lead) are texture, porosity, and permeability. These characteristics are not independent of one another and must be addressed as a whole when considering their effect on the

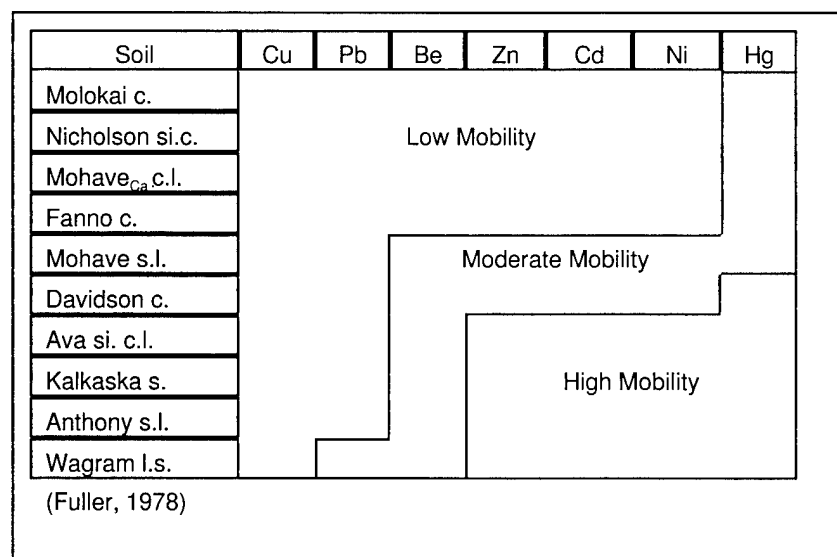


Figure 2. Relative mobility of cations in soils.

movement of contaminants. These parameters together with chemical and biological variables, discussed later in this paper, determine to what degree pollutants are attenuated and retained in a particular soil.

## Soil Texture

The percentage of sand, silt, and clay within a soil determines its texture. The diameters of these particles are 2 to 0.05 mm for sand, 0.05 to 0.002 mm for silt, and less than 0.002 mm for clay. When siting a landfill, it is important to determine the predominant soil texture to assess the location's ability to contain potential pollutants. Disposal sites located in medium-textured soils, such as those classified as loams by the U.S. Department of Agriculture (50 percent sand and 50 percent silt and clay with about equal proportions of each) appear to be the most desirable. As the soil texture becomes finer, the grain surface area increases, resulting in a greater pollutant sorption capacity. The ratio of a sphere's surface area to volume illustrates this relationship:

$$\frac{\text{Area}}{\text{Volume}} = \frac{4\pi \cdot r^2}{\frac{4}{3}\pi \cdot r^3} = \frac{3}{r} \quad [\text{Eq 1}]$$

When clays become hydrated, they expand to different degrees. The clay expansion effectively increases the surface area where metals can accumulate. Therefore, the degree to which a clay expands influences its ability to retain pollutants. Soils with a high clay content drain slowly, resulting in an accumulation of leachate. This accumulation of leachate is undesirable since it can exit the top of a landfill and also may inhibit biodegradation of waste. On the other hand, sandy soils characteristically allow unrestricted flow of leachate and have little capacity to retain pollutants or even fine suspended matter. These properties of sand increase the risk of groundwater contamination (Fuller 1985). Soils composed of all sand or all clay are therefore undesirable, and many experts recommend locating a site where the predominate soil texture is similar to loam.

One of the most important soil parameters that affects the attenuation of pollutants is the clay fraction. Small differences in clay content can make appreciable differences in the soil's capacity of the soil to attenuate heavy metals and other pollutants (Fuller 1985). Clays have very large surface areas, reduced permeability (increasing contact time for reactions to occur), and typically have large cation exchange capacities (Christensen 1989). Clays are aluminosilicates composed of silicon and aluminum atoms arranged in a "sheet" structure. The arrangement of these sheets determines to a large extent the physical and chemical properties of a

particular clay. Clays are typically classified according to their structure, 1:1, 2:1 and 2:2. The 1:1 structure is composed of one  $\text{SiO}_4$  sheet and one  $\text{AlO}_6$  sheet, which together constitute a layer. Hydrogen bonding between the layers is strong enough to prevent ions from entering between the layers, creating a relatively stable clay. A 2:1 clay has two  $\text{SiO}_4$  sheets and one  $\text{AlO}_6$  sheet.

In some of these clays, the  $\text{Al}^{3+}$  may be replaced with  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ . The incorporation of these atoms alters the charge on the clay. Ions such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  may also be found between the layers, along with water, helping hold the structure together. The greater bond instability of incorporated cations also confers an electron donor character that makes possible exchange reactions with metal cations or dipolar molecular (Avogadro, 1993). The third clay structure, 2:2, is composed of two aluminum and silicon sheets. The 2:1 structure typically has a greater ability to retain pollutants than the other two structures. The capacity of clays to concentrate metals has been observed to follow this general trend: montmorillonite (2:1 expanding clay) > vermiculite (2:1 limited expanding clay) > illite (2:1 nonexpanding clay) > chlorite (2:2 clay) > kaolinite (1:1 clay) (Fergusson 1990). The cation exchange capacity to a large degree determines the quantity and type of pollutants that can be retained by clays.

The cation exchange capacity of a soil is primarily determined by the surface charge on the clay material. There are two mechanisms of charge generation on clay particle surfaces. Structural or constant charges are associated with the surfaces of the phyllosilicate clay materials, whereas pH-dependent, or variable, charges are associated with the protonation of surface oxygens, and deprotonation of hydroxyls at the edges and surfaces of minerals within the clay (Appelo 1993). The association of protons with a surface creates a positive charge; the dissociation of protons under less acidic conditions results in a negative surface charge (Evans 1989). The permanent structural charge is caused by substitution of  $\text{Si}^{4+}$  atoms by other elements. The substitution of elements such as  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  or  $\text{Li}^+$  in the clay structure will result in a negative charge. A positive charge may also be generated by substitution of atoms. However, the positive charge resulting from the imperfections is always neutralized by the negative charges within the clay lattice structure (Evans 1989).

The attenuation capacity is not the only property that should be considered when choosing a material for a landfill liner or disposal site. The stability of the material, swelling potential, porosity, permeability, and other properties that depend on the soil texture need to be considered. For example, leaks in clay liners appear more frequently with the montmorillonites under wetting and drying conditions, than with nonexpanding lattice clays such as kaolinite and illite (Fuller 1985). Soil

texture is an important variable to consider when assessing the pollution risk at existing or proposed disposal sites.

## Porosity and Permeability

Porosity and permeability are directly related, and control the rate at which water moves through the subsurface. Soil with low permeability and porosity can lengthen the flow period and act as a natural defense by retarding the movement of contaminants (Ferrara 1984). The slow movement of water increases the time for chemical and biological reactions to occur that may reduce the mobility of pollutants. Therefore, the solution flux through soil affects the attenuation of metals (Fuller 1978). Total porosity is the ratio of void space to total volume expressed as a percentage. Effective porosity is also a ratio, but one that uses the volume of interconnected pore spaces through which water can move instead of total void space. Effective porosity is usually somewhat less than total porosity and gives a better indication of the rate at which water will move through the subsurface. Total soil porosity can be related to bulk density and particle density by:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \quad [\text{Eq 2}]$$

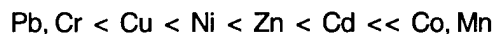
Permeability, like porosity, depends on the presence of pore space. Permeability of a porous medium refers to the ease with which a fluid passes through it, and depends on the viscosity and specific weight of the fluid. The permeability of a geologic formation depends on a variety of physical factors, including porosity, particle size and size distribution, the shape of the particles, particle arrangement, and secondary features such as fracturing and dissolution (Barcelona 1990). The soil at a landfill is often disturbed resulting in a homogeneous mixture free of secondary features often found in natural soils (Fuller 1977). Permeability is calculated using the effective velocity, distance, and headloss. The U.S. Geological Survey has determined the permeability for gravel through which water, under a gradient of 2 m/km, would move at the rate of 18 m/day, and for a clay through which, under the same gradient, the rate of movement would be 0.3 m/30,000 years. Flow rates in most aquifers range from a few feet per day to a few feet per year (Miller 1980). Clay liners are typically compacted so that the in situ permeability is not greater than 10<sup>-7</sup> centimeters/second (Harris 1988). A sound understanding of physical soil parameters that affect the movement of contaminants is needed to make sound disposal decision.

## 5 Metal Transport

### Mobility

Metals generally have limited mobility in the subsurface because sorption reactions with soil materials and precipitation remove metal ions from solution readily. The physical characteristics of a soil, as discussed above, along with chemical and biological reactions determine the rate of metal migration at disposal sites. Chemical and biological factors that control the transport of metals include hydrolysis, sorption, cosolvation, ionization, precipitation, and biotransformation. These reactions can mobilize or stabilize pollutants in the subsurface under various conditions. Reactions that stabilize contaminants retard the flow and minimize the risk of groundwater pollution. Therefore, to minimize the movement of heavy metals in a landfill environment, it is desirable to minimize the permeability and rate of diffusion, and maximize the retardation (Bonaparte 1990).

Under certain conditions, heavy metals in an aquifer can be highly mobile and threaten drinking water sources (Miller 1980). Because of lead's toxicity, it has the potential to harm human health if it enters an aquifer and remains mobile. In the soil, lead typically has a very low mobility (Cheremisinoff 1993). This is because lead forms slightly soluble salts and binds tightly to clays and organic matter in the terrestrial environment. This is supported by the observation that there is normally less lead in groundwater than in rain (Griffin 1975). During the 1970s Griffin and Shimp showed that clay materials could remove approximately 99.8 percent of the lead in typical landfill leachate (Chittaranjan 1986). Usually the mobility of the metals increases in the following order:



However, this order can deviate according to the presence of dissolved organic matter and redox conditions (Vernet 1991). Any changes in soil, whether natural or as a consequence of human activities, that increase the mobilization of pollutants into drinking water supplies must be considered as a potential health risk (Cresser 1993). Because the design of a landfill involves excavation below the earth's surface, the normal soil buffering thickness that protects groundwater and prevents the lateral movement of solutions is lessened (Fuller 1985). Without this protection,

aquifers become vulnerable to contamination by lead and other contaminants. In fact, there is some evidence that lead may be leached from highly contaminated soils and threaten groundwater supplies (WHO 1989). Complexation with mobile colloids present in leachate may be responsible for the observed transport of lead (Bedient 1994).

Physical parameters that affect the movement of metal are referred to as conservative transport mechanisms. Nonconservative transport mechanisms involve biological and chemical reactions that affect the movement of metals. Both mechanisms are interrelated, and the impact of one on the attenuation of metals cannot be considered without accounting for the other. For example, precipitated metals may decrease the permeability of a soil. In this case, a nonconservative chemical mechanism influenced the conservative transport of a solute. The conservative and nonconservative parameters that affect the movement of lead are discussed below.

## Conservative Substances

Inert substances are often referred to as conservative because they are not chemically or biologically reactive. These substances are commonly used as tracers to determine the movement of a solvent through a porous medium because they are not hindered by biological or chemical influences. Advection, dispersion and diffusion are the primary mechanisms by which conservative contaminants move through soil. Typically, a conservative pollutant will move at approximately the same velocity as the solution it is dissolved in, except when the velocity approaches zero.

Advection is the migration of fluid due to a hydraulic gradient. This transport mechanism will cause a conservative solute to move at the average linear velocity of the groundwater (McTernan 1990). The average linear velocity is less than the microscopic velocities of water molecules moving along individual flow paths, due to tortuosity. This mechanism is generally considered the most important parameter governing pollutant transport (Ferrara 1984). Advection depends on the velocity of the solvent, which in turn depends on the piezometric head, distribution, permeability, and effective porosity. Darcy's law (Equation 3) is commonly used to model advection. The calculated velocity is used in solute transport equations.

$$v_x = -\frac{K}{n_e} \cdot \frac{\delta h}{\delta x} \quad [\text{Eq 3}]$$



Dispersion is the spreading of particles in both the directions of solvent flow and transverse to it (Appelo 1993). Mechanical dispersion is caused by velocity variations in the fluid. In natural porous materials, the pores possess different sizes, shapes, and orientations. Velocity distributions exist within the pore spaces such that the rate of movement is greater in the center of the pore than at its edges (Barcelona 1990). These variations occur within individual soil pores on a microscopic scale and within soil layers because of permeability variations on a larger scale (McTernan 1990). A concentration gradient must be present for dispersion to take place. Dispersion depends on the mean flow velocity and is greater in the direction of flow (Ferrara 1984). Dispersion causes sharp fronts to spread out and results in the dilution of the solute at the advancing edge of a contamination front.

The term diffusion is used for the random movement of particles in stagnant water (Appelo 1993). The driving force for molecular diffusion is a chemical potential. Diffusion occurs by transfer of kinetic energy between the water and solute by molecular collision (Brownian motion). The rate is governed by the temperature and the type of solute, and exhibits no preferred direction of mixing (Avogadro, 1993). Molecular diffusion is relatively unimportant except when the flow rate of the groundwater is very low, or the concentration of the contaminant is high (Miller 1980). This mechanism can be modeled using Fick's Law (Equation 4):

$$F = -D \frac{\delta C}{\delta x} \quad [\text{Eq 4}]$$

The equation states that contaminants move relative to the mixture in the direction of decreasing concentration. Activities, instead of concentrations, should be used to calculate the potential gradient, since differences in the chemical potential are the real driving force (Appelo 1993). It can be assumed that, in most situations, the concentration is approximately equal to the activity. This transport mechanism may be significant in relation to solute movement through liners. The steady state flux of contaminants through a liner, whose sorptive capacity has been exhausted, may be significant and may cause extensive groundwater pollution (Appelo 1993).

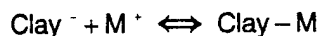
## Nonconservative Substances

Nonconservative solute migration depends not only on advection, diffusion, and dispersion, but also on chemical and biological processes. Nonconservative contaminants typically migrate more slowly than the seepage velocity of the solvent; this phenomenon is referred to as retardation. The movement of the solute relative to the solvent velocity is expressed as a ratio called the retardation factor. Retardation

factors range from 1 to over 10,000, depending on the solute and geologic environment (McTernan 1990). Retardation/attenuation can be attributed to sorption by organic and inorganic substances, precipitation, hysteresis, and biotransformation (Bonaparte 1990).

Heavy metal transport in soils and aquifers is predominantly controlled by sorption. Sorption is comprised of absorption (where the contaminant is assimilated) and adsorption (where it is concentrated on the surface). In most instances, the specific solute/soil interactions are unknown. Sorption partitions contaminants from the soluble phase onto the soil matrix, resulting in retarded fronts. Both organic and inorganic substances can retain lead by sorption (Davis 1991). Contaminant sorption can result from electrostatic attraction, ion-exchange, and complexation with oxides and organic molecules in the soil. The ability for clay to accumulate heavy metals by sorption is influenced by the number of bonding sites available, pH, metal species, expansion potential, and oxide concentration (Ferrara 1984). Organic sorption depends on pH, ionic strength, species, and redox potential. Sorption has been observed to follow the order: montmorillonite > humic materials > kaolinite > allophane > imogalite > halloysite, iron oxides (in most situations). The primary mechanism for the attenuation of lead is sorption, until the pH is reached where  $\text{Pb}(\text{OH})_2$  begins to precipitate (Fergusson 1990).

The sorption of lead may occur as a result of electrostatic attraction and van der Waals forces, which are nonspecific in character. Oppositely charged metallic counter-ions from solution are attracted to charged soil surfaces.



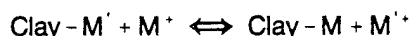
An electric double layer is set up between the charged surface (e.g., on a clay or Mn/Fe hydrous oxide), and the sorbed material, which may be an ionic species or a polar species such as water. The attraction of oppositely charged particles to a surface can change the surface's net charge and influence subsequent processes. This is the reason clays have variable charges due to protonation of surface oxygens, and deprotonation of hydroxyls (Appelo 1993). The zero point charge is used to estimate the pH at which the surface charge will be neutral (Fergusson 1990). The zero point charge occurs when a particle's surface oxygen is protonated just enough to compensate for broken bonds and a small internal charge (Appelo 1993). Consequently, the surface charge changes from positive to negative at pH's below or above the pH of zero point charge. The clay materials kaolinite and montmorillonite

have zero point charges lower than the pH range of 6.5 to 8.5 normally found in groundwater, and these materials typically behave as cation exchangers only. This is the reason they are so effective at retarding the movement of lead. Table 10 lists the pH at which the zero point charge occurs in some selected materials.

The ability of a soil to hold and exchange cations is referred to as its cation exchange capacity. Cation exchange is the principle method by which organics and clays retard the movement of metals. Soil particles possess an electrostatic charge as a consequence of atomic substitution within their structural lattice (permanent charge) and as a result of hydrolysis reactions on broken edges of the lattices and the surfaces of oxides, hydroxides, hydrous oxides, and organic matter (pH-dependent charge) (Carter 1993). When all potential adsorption sites on a surface become occupied by electrostatic attraction, ion-exchange becomes the primary sorption process. The ion-exchange process removes constituents from solution while at the same time displacing others that have a lower affinity for the sorption site back into solution.

**Table 10. pH where zero point charge occurs in selected materials.**

Material*	pH at zero-point charge
$\alpha\text{-Al}_2\text{O}_3$	9.1
$\alpha\text{-Al(OH)}_3$	5.0
$\gamma\text{-Fe(OH)}_3$	6.7
$\text{Fe(OH)}_3$ amorphous	8.5
$\text{MnO}_2$	2-4.5
$\text{SiO}_2$	2.0
Kaolinite	4.6
Montmorillonite	2.5
Calcite	8-9.5
* Source: Fergusson 1990.	



In some cases, the release of ions may aggravate the pollution problem (Barcelona 1990). For example, lead is known to be adsorbed readily onto clay minerals and is replaced only with difficulty (Lovering 1976). Therefore, lead could displace a more toxic compound that is not as strongly attracted to the sorption site. This may release the compound into a drinking water source, threatening human health. In most instances,  $\text{Ca}^{2+}$  is released resulting in a "hardness halo." Lead sorption to clay is favored by a factor of two or three over calcium (Rolfe 1977). Halo's are commonly observed in field monitoring wells at landfills, and are an indication of ion-exchange reactions (Griffin 1978).

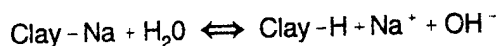
In fresh water, the dominant cation is  $\text{Ca}^{2+}$ ; for salt water it will be  $\text{Na}^+$ . The exchange coefficient for almost all heavy metals is greater than one for exchange with  $\text{Ca}^{2+}$ , so the sorption of heavy metals is favorable.  $\text{Na}^+$  is less strongly sorbed than calcium as long as the total salt concentration remains below 2 moles/L. Therefore, it can be assumed that heavy metals are also favorably sorbed in salt water (Appelo 1993). The ability of one cation to displace another can be estimated

using general rules of thumb. Cations that do not form covalent bonds with the clay surface form only a weak association between the adsorbed ion and the soil particle. Because of the weak association, the adsorbed ions are easily exchanged with other cations that form similar complexes with the surface (Evans 1989). The strength of attraction between a clay and cation depends on the charge of the ion,  $M^{3+} > M^{2+} > M^+$ . When two cations have the same charge, the relative strength is determined by their hydrated ionic size, the largest being more strongly attracted (Fergusson 1990). Earth-alkaline cations have a tendency up to six orders of magnitude less to displace protons from  $Al_2O_3$  and  $TiO_2$  than heavy metals such as  $Pb^{2+}$ . The ion exchange coefficients are generally about equal for heavy metals and earth-alkaline ions, but the tendency of heavy metals to displace protons from oxide surfaces is more than a 1000 times greater (Appelo 1993).

Cation exchange reactions are rapid, stoichiometric, and reversible. The capacity of a material to sorb ions is measured in milliequivalents per 100 grams of solid at pH 7 (Barcelona 1990). The pH is specified when reporting the cation exchange capacity of a soil because it strongly affects a soil's ability to retain ions. Ion exchange capacity is very dependent on pH; metal ions exchanged onto geologic materials readily at neutral pH may be displaced by hydrogen ions at lower pH values (Barcelona 1990). Clays in which  $Si^{4+}$  atoms have been replaced by  $Al^{3+}$  are anionic, and at elevated pH, the hydroxyl groups lose protons or the protons are replaced with metal ions. Heavy metals actively compete with protons for surface sites even at low concentrations.



In a pH-buffered soil, the liberated hydroxide ions are immediately neutralized by hydrogen ions. To maintain the activity of  $H^+$ , more protons must pass into solution from cation exchange sites, and an equivalent amount of base cations must be adsorbed in their place. The exchange of cation can also directly affect the soil pH. Frequent leaching of soils in humid environments results in protonated clays and low pH values. In arid climates, cations such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ , and  $K^+$  tend to raise the pH when they are released from a clay.

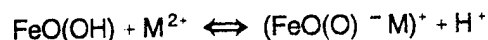


Soils commonly can retain 40 to 72 percent of their cation exchange capacity before leaching occurs (Boggess 1976). At equilibrium, the maximum lead sorption is nearly 100 percent of a soil's cation exchange capacity (Griffin 1977). After the

capacity of the soil is reached, there will be no attenuation of lead. Therefore, a permanent or long-lasting pollution load will ultimately result in saturation of the exchange and adsorption capacity and result in break-through of the pollutant (Jousma 1989).

The hydrous oxides of manganese, aluminum, and iron are responsible for the chemisorption and co-precipitation of heavy metals. In addition to their surface complexation properties, they exhibit high redox activity and often occur as a layer, coating the surface of other minerals (Avogadro 1993). Oxides attached to soil particles exist in amorphous or microcrystalline forms and exhibit a high specific surface area; up to 300 m<sup>2</sup> per gram (Miller 1980). The primary iron compounds are Fe(OH)<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> (magnetite), FeO(OH), and α-FeO(OH) (goethite). Goethite is the most thermodynamically stable iron oxide in soils. The major manganese compounds are b-MnO<sub>2</sub> (pyrolusite), d-MnO<sub>2</sub>, Mn<sub>7</sub>O<sub>13</sub>•5H<sub>2</sub>O (birnessite), MnO(OH) (manganite) and Na<sub>4</sub>Mn<sub>14</sub>O<sub>27</sub>•9H<sub>2</sub>O (mango-manganite). The most stable manganese oxide is pyrolusite. Gibbsite, α-Al<sub>2</sub>(OH)<sub>6</sub>, can also form complexes with metal cations (Evans 1989). The ability of these substances to sorb metals is governed by soil pH, redox, and ionic strength.

Some studies have suggested that the Fe/Mn oxides play a more important role in the complexation of lead than organic matter. The specific adsorption complex involves covalent bonds. Therefore, the adsorbed ions are not easily displaced (Evans 1989). Heavy metals attach to the hydrous oxides and become incorporated into the lattice of the hydrous oxide by removing a proton (Fergusson 1990). Adsorption onto mineral surfaces occurs most readily with metals that hydrolyze in water.



This and other simultaneous pH-dependent reactions within the soil affect the ability of oxides to sorb metals. The effect of pH on metal mobility may also be an indirect consequence of microbial activity, which in turn controls the oxidation and reduction of iron and manganese (Lovering 1976). Mn(II) and Fe(II) are both mobile and form insoluble species in the oxidized states Mn(III), Mn(IV) and Fe(III). The minerals of Mn, especially the Mn oxides, are very soluble in soils because of their susceptibility to hydrogen ion activity and redox changes (Fuller 1985). Mn-oxides are first reduced followed by Fe-oxides. If Mn- and Fe-oxides were simultaneously reduced by organics, the resulting Fe<sup>2+</sup> would reduce Mn-oxide by a fast reaction and precipitate as Fe(OH)<sub>3</sub> (Appelo 1993). Ionic strength also affects the sorption of lead into the lattice. Lead sorption decreases with an increase in Cl<sup>-</sup> ion concentration,

due to the formation of lead chloride complexes (Fergusson 1990). However, the chloride complex will not be significant in solutions having less than about 1,000 mg/L of chloride (Lovering 1976). There is some indication that hydrous manganese oxide is more effective at complexing lead than hydrous ferric oxide or hydrous aluminum oxide (Rolfe 1977).

The organic components of a disposal system are an extremely diverse group. Compounds commonly found include carbohydrates, amino acids, phenolic and quinonic compounds, organic acids, nucleic acids, enzymes, porphyrins and other heterocyclic compounds, lipids, terpinoids, and humic materials. In addition, organic industrial products may be present: e.g., oils, plasticizers, polymers, solvents, and pesticides (Lovering 1976). Organic matter can be roughly divided into a humic and nonhumic fraction. The nonhumic fraction consists of products such as fats, waxes, oils, resins, water soluble polysaccharides, hemicellulose, cellulose, and proteins. Humic matter on the other hand is a relatively stable by-product of the microbial transformation of a great variety of biochemical compounds derived from dead cells and extracellular products of various organisms. The humic components tend to make up the largest proportion of the soil organic matter (Cresser 1993). Humic matter can also be separated into two fractions: those that are and those that are not soluble in an alkaline solution. Alkaline-soluble humic matter is better known as humic and fulvic acids (HA and FA). Material that is not soluble under any pH value is known as humine. Humic and fulvic acids commonly affect the movement of lead to a greater extent than any other organic substance typically found in MSW landfills.

Humic acids all have aromatic nuclei in the form of flat lattices of cyclical polymerized carbon. The basic structure consists largely of condensation products of compounds such as catechol, syringaldehyde and 3,5-dehydroxybenzoic acid. Side chains are connected with various functional groups such as carboxyl, phenolic and alcoholic hydroxyl, methoxyl, carbonyl, and quinone groups (Vernet, 1991). Elemental analysis of humic acid has revealed that they are composed of about 50 percent carbon, 40 percent oxygen, 5 percent hydrogen, 3 percent nitrogen and 1 percent phosphorus and sulfur (Cresser 1993). Their molecular weight ranges from 700 to > 2,000,000, the lower mass representing younger material. Humic acids are insoluble in acidic solutions, but soluble at high pH (Avogadro 1993).

Fulvic acids contain aromatic rings that form an open structure in a two- or three-dimensional array. The open structure is held together, at least partly, by hydrogen bonds among the functional groups. The functional groups identified in the humic acids have also been identified in fulvic acids (Vernet 1991). Fulvic acids typically contain less carbon and more nitrogen and oxygen than humic acid (Cresser 1993).

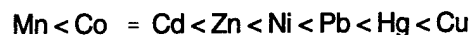
Fulvic acids are also less condensed and remain in solution. Therefore, metal ions that coordinate with them are solubilized (Fergusson 1990). Fulvic acids are soluble over a wide pH range (1-13) (Avogadro, 1993). Fulvic acids appear to be composed mainly of microbial metabolites and younger material not highly associated with the mineral fraction. However, all material, old and young, can be part of the fulvic acid fraction (Carter 1993). High HA:FA ratios found in surface soils of moist environments are believed to reflect more intense humification as a result of greater biological activity (Carter 1993).

The interaction of metals with humic materials has been classified into three categories: formation of heteropolar salts (an ion exchange phenomenon between strong bases and humic material), formation of coordination complexes, and formation of adsorption complexes with nonsilicate sesquioxides (adsorption of humus on sesquioxide gels) (Lovering 1976). Parameters that influence the transport of metal-soluble organic matter are the stability constant of the metal-humic complex, the pH (which determines the competition from carbonate and hydroxyl ligands), and the major ion concentration (Vernet 1991). The stability of trace element chelates is influenced by the nature of both metal ion and ligand, number of rings formed, and the soil pH.

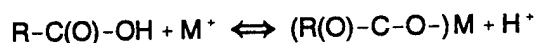
The donor atom in most organic complexes is oxygen; metals that readily form hydroxo-complexes in water can be expected to form relatively strong complexes with organic ligands (Evans 1989). The leaching of Cr, Cu, Fe, and Pb is directly related to the solubility of organic matter because it forms a stable complex with metal ions (Vernet 1991). The least retardation of lead in the landfill environment occurs during the acetogenic phase, when the concentration of volatile fatty acids is the greatest. The pH is important in determining the solubility and the state of hydrolysis of the metal cations and therefore also their ability to complex with humic or fulvic acids. During the acetogenic phase, the pH is low and there is a high concentration of soluble organic matter resulting in elevated levels of soluble lead (Bolter 1977). Fatty acids not commonly associated with the movement of lead have also been found to mobilize lead in synthetic landfill leachate (Vernet 1991). Under strict reducing conditions, a neutral pH, and a relatively low organic load, the requisites for immobilization of metals are created in landfills (Christensen 1989).

Humic and fulvic acids behave as negatively charged species due to the ionization of their acidic carboxyl and hydroxyl groups, which depends on the pH. At elevated pH, they can attach to positively charged particles like metal ions and form stable

complexes. The stability of metal-humic acid chelates formed between metal ions and ligands are reported in the following order as determined by paper chromatography testing:



With increasing ionic strength, the stability of metal-fulvic acid complexes decreases. This may be attributed to increased competition between the different ions in solution to complex with organic matter. Specific conductivity is a parameter that can be directly correlated to the ionic strength of a solution and is therefore correlated to the increase of lixiviation of metals due to the decrease in activity coefficient (Christensen 1989). The cation exchange capacity of soil humus can exceed 300 milliequivalents per hundred grams. It has been estimated that between 20 and 70 percent of the soil's cation exchange capacity results from organic matter (Cresser 1993).



At low pH, the humic acid molecules are aggregated into colloidal particles with very little charge. In this environment, the molecules precipitate. In this way, the fulvic and humic acids can be separated. If the pH is increased, the negative charge on the molecule increases and dissociation occurs. Because of this phenomenon and because fulvic acids have more carboxyl and hydroxyl functional groups, they can complex more heavy metals over a greater pH range than humic acids. The different affinities of organic groups for trace element ions generally follow the order: carbonyl < ether < carboxylate < ring N < azo < amine and enolate. The strength of the bond is independent of the atomic weight, the atomic number, ionic radius, or the hydrated radius of the retained ion (Evans 1989).

Humic molecules often attach to solid components of the soil matrix such as clay particles (Cresser 1993). Clay-humic complexes form when humates are absorbed to clay material by polyvalent cations such as  $\text{Fe}^{3+}$  or  $\text{Ca}^{2+}$ , and by association with hydrous oxides, either through coordination or anion exchange (Fergusson 1990). The complexation can occur between humic materials containing lead and clay. This reaction effectively removes lead from solution and is referred to as coprecipitation. It has been observed that the surface charge of alumina can be gradually modified by sorption of humic acids to the extent that the electrophoretic behavior of the humic acid-covered particles approximates that of pure humic acid colloids (Avogadro 1993). The positive sites on sesquioxides will not exist at soil pH values above 8, therefore clay-humate complexes are less likely to form in alkaline soils



(Cresser 1993). At high pH, substantial dissociation of phenolic and carboxyl groups on the organic matter occurs, increasing its solubility (Cresser 1993).

Baker observed that the solubility of lead minerals in a 0.1 percent humic acid solution increased sharply compared with the solubility in carbon dioxide-saturated water. Bolter and Butz used a lower concentration of HA and a higher pH; their results agreed with those collected by Baker (Bolter 1977). Aquatic mobilization and partial removal of otherwise insoluble lead compounds from polluted areas can be attributed to the reactivity of humic material and decreased pH values associated with the presence of HA (Boggess 1976). Newly formed soluble organic substances can compete with clay and organic colloids for metals, resulting in increased lead solubility (Rolfe 1977). The presence of fulvic acid has been found to increase the rate of solution of lead sulfide 10 to 60 times over a water solution at the same pH that did not contain the humic substance (Lovering 1976). Organic-metal complexes can also lower the activity of the Pb in solution, resulting in a reduced potential gradient for sorption to inorganic materials (Griffin 1978).

Recent results obtained by Stevenson at Illinois show rather rapid downward movement of lead in a Drummer silt loam soil, where plots were established by Baumhardt and Welch has received treatments of lead ranging from 0 to 3,200 kg/ha in 1969. After six years, the maximum lead penetration was 46 to 61 cm for the 800 kg/ha rate; 61 to 76 cm for the 1,600 kg/ha rate; and 76 to 91 cm where 3,200 kg/ha had been added. In addition, both organic matter and total nitrogen increased on land-amended plots where 20 tons per acre of ground corn cobs were added in 1973 and 1974. These increases appeared due to enhanced preservation of stable humus, perhaps because newly formed humic and fulvic acids were protected from microbial attack by the formation of complexes with the added lead (Boggess 1976).

The reversible nature of sorption can have significant environmental consequences. Both organic and inorganic materials can release sorbed cations if the ionic composition or pH is altered in a disposal environment (Griffin 1977). Large quantities of hazardous pollutants can be released into solution by the addition of hazardous or nonhazardous solutes at a disposal site because of competition for sorption sites (Griffin 1978). The potential for this to occur must be considered when designing or evaluating a landfill.

The dominant removal mechanism for metal cations when  $\text{pH} < 5$  is sorption, and when  $5 < \text{pH} < 6$ , it is precipitation (Ferrara 1984). Precipitation of new mineral phases occur when the chemical composition of the soil solution becomes supersaturated with respect to insoluble precipitates. Solubility of a solid indicates whether dissolution or precipitation reactions are favored. Precipitation effectively

removes lead from solution because lead precipitants have a relatively low solubility in pure water. However, the solubility of a solid in a solution can be altered when various ions/substances are present. Precipitation can also alter conservative transport mechanisms in a landfill environment. For example, precipitated material may be trapped in the pore spaces of the soil and aquifer media, clogging the pore spaces and limiting flow. This phenomenon, filtration, can reduce the hydraulic conductivity of the material (Barcelona 1990). The common precipitants of lead are oxides, hydroxides, oxyhydroxides, and carbonates; sulfides, phosphates, and silicates are generally less important. Typically, the most important inorganic ligand in the geotechnical environment is the OH<sup>-</sup> anion (Evans 1989).

Lead tends to form secondary lead sulfates and carbonates in soils overlaying mineralization (Hutchinson 1987). The precipitation of metallic carbonates and sulfides in soil is controlled not only by the solubility products, but also by the partial pressure of carbon dioxide and hydrogen sulfide (Evans, 1989). Lead sulfate and carbonate are both used as pigments in paint; the latter is considered more toxic (Gooch 1993). Sulfides are the most important compounds for the precipitation of metals. Increasing the oxidizing characteristics of an environment results in the formation of relatively insoluble lead complexes, e.g., PbSO<sub>4</sub> (Fergusson 1990). When the redox potential in the soil is low, HS<sup>-</sup> ions are formed. At high redox values, sulfide minerals will be oxidized to SO<sub>4</sub><sup>2-</sup>. Because protons are produced, precipitants will typically dissolve. Therefore, the stability of sulfides depends on the oxidation or reduction state of the soil (Evans 1989). At very low sulfide concentrations, carbonates and hydroxy-carbonates play a fundamental role in the precipitation of metals (Christensen 1989). The pH and carbonate speciation are interdependent, a function of not only the ionization equilibria for the carbonate species and water, but also of strong bases added through the dissolution of carbonate and silicate materials (Bedient 1994).

The hydroxo-complexes of some metals, especially Al<sup>3+</sup> and Fe<sup>3+</sup>, also play an important role in controlling the mobility of metals. The formation of Al(OH)<sub>4</sub><sup>-</sup> and Fe(OH)<sub>4</sub><sup>-</sup> at neutral and alkali pH's increase the solubility of metal hydroxides (Evans 1989).

The pH of the geologic materials and the waste stream have a major influence on actual retardation. In general, lead is more mobile in acid soils than in alkaline soils since it tends to be leached out of the former and to form residual concentrations in the latter (Lovering 1976). Hydrolysis reactions can precipitate hydroxides and oxyhydroxides. The pH determines the relative distribution of precipitating ions (sulfides, carbonates, and hydroxides), which determine solubility and reactivity. Clays reduce the pH at which metal hydrox species may precipitate

(Fergusson, 1990). A general characteristic of heavy metal compounds prevailing in the ecosphere is that their solubility greatly depends on the pH of the solution, with a strong increase of the solubility with decreasing pH.

Factors that regulate the solubilization of metals are pH, redox potential, complexing and ionic strength (Christensen 1989). Solubilization and movement of some metals in soils is a continuing, but usually very small process (Fuller 1985). Only at a pH range less than 5 does the mobilization of heavy metals become a problem of actual relevance. Carbonates and carbonate-containing minerals of both soils and geologic formations are readily susceptible to dissolution by acids (Fuller 1985). Carbonation can free heavy metals from carbonates, giving concentrations in solution that are higher than expected. Solutions of high ionic strength may retain substantially more lead in solution than do more dilute waters. Ion-pairing effects also become increasingly important at high ionic strength (Lovering 1976). Generally, the solubility of a solid increases with increasing ionic strength.

Research in the early 1960s reported that lead sorbed on montmorillonite was rendered nonexchangeable by drying the clay (Boggess 1976). Wetting and drying of 3- and 5-year-old MSW leachates under a vacuum resulted in a hysteretic effect where all of the soluble constituents of TOC, Cd, Ni, Zn, and Fe did not return into solution on rewetting. It was concluded that drying or cycling through dehydration/rehydration could lower the solubility of certain contaminants in dilute aqueous solutions or leachates such as those generated in MSW landfills. Further research has confirmed that dehydration does contain a valid and measurable hysteretic effect on rehydration. However, the practical significance of this has yet to be demonstrated under field conditions (Fuller 1985).

Biological reactions may play an important role in the transport of lead. The most significant reaction affecting lead may be methylation. Methylation refers to the transfer of a methyl group from one compound to another. The process may occur biologically or abiotically (one which does not directly involve a biological system). Lead in soil may be biomethylated, producing volatile  $(CH_3)_4Pb$  and  $(CH_3)_{4-n}Pb^{n+}$ . The first suggestion of the methylation of inorganic lead was reported in 1975. The work has been challenged, reinterpreted, and also confirmed, leaving some doubt as to whether biomethylation occurs. The weight of evidence however, tends to favor the occurrence of the process. A study conducted at the University of Illinois isolated a number of soil bacteria that were able to solubilize and accumulate lead from highly insoluble salts (e.g.,  $PbS$ ) (Rolfe 1977). Biological uptake of lead was found to depend on the presence of a nutrient source. Bacteria that are reported to methylate heavy metals are commonly unicellular, rod-like in shape, and heterotrophic. Species suspected of methylating lead are *Acinetobacter*,

*Aeromonassp*, *Alcaligenessp*, *Escherichia coli*, *Flavobacterium sp*, and *Pseudomonas sp* (Fergusson 1990). The flux of organometallic lead is small compared with that of inorganic on a global basis (Hutchinson 1987).

Research indicates that the presence of lead influences biological reaction occurring in the soil. Lead biochemically reacts with enzymes in living material. The binding of lead to enzymes and the consequent inhibition of enzymatic activity will affect the biological reactions that take place in the environment (Lovering 1976). Therefore, lead may be responsible for limiting the enzymatic activity of microbes causing organic matter to accumulate in soil (Fergusson 1990). Landfill design relies on biological activity to stabilize organic matter. If inhibition occurs, the landfill will not operate correctly. Biological inhibition may be prevented if the soil contains sufficient quantities of humic material. Active sites on the humic material will preferentially bind to the cation preventing it from binding to enzymes. The effect of lead on the biological health of a landfill should be considered before land disposal of lead-contaminated waste.

Lead can be mobilized by a variety of environmental parameters. It is impossible to predict the actual influence of chemical and physical reactions on the solubility of lead, but general trends have been observed. Elevated pH is commonly associated with increased attenuation of heavy metals. Oxidizing conditions favor attenuation as opposed to a reducing environment. The potential for metals to be attenuated by soil particles increases as the surface area becomes greater. Attenuation often increases as the solute flow becomes slower. Therefore, advective flow is an important parameter when evaluating the potential for metal mobility. Organic colloids frequently increase the mobility of metals. However, larger organic particles may increase the attenuation of metals because of their high cation exchange capacity. Low ionic strength is often associated with increased attenuation. The exception to this observation is the formation of precipitants with inorganic ligands such as sulfides and chlorides. Soils with significant hydrous oxides are known to have great attenuation capacities for metals. The wetting and drying of a soil generally decreases the mobility of lead. The mobility of metals will be accelerated in anaerobic soil environments. These general trends will have exceptions, but they can be used to get a rough estimate of a soil's attenuation potential. Without experimental and field data, it is impossible to evaluate the actual transport of metals at a unique disposal site.

## 6 Theoretical Modeling

### Models

A model provides a simplified analogy for a natural phenomenon. Models that predict the transport of metals are vital for the proper management of solid waste. Throughout the life cycle of a disposal site, models can be used to help landfill operators protect the environment. Models can assess the potential for existing and future landfills to contaminate potable water supplies and guide in the clean-up of polluted sites. Only through the use of advanced solute transport models, accounting for ion-exchange selectivity, precipitation, and complexation, can acceptable predictions of cation behaviors be obtained (Christensen 1989). The use of hydrogeochemical models to predict actual transport of metals is limited by a lack of kinetic and thermodynamic data describing reactions that occur in the environment (Davis 1991). The comparison of observed lead concentrations with theoretically calculated ones can never be expected to give more than an approximate indication of the processes involved. The three mineral properties usually most important in modeling the transport of contaminants in groundwater are hydraulic conductivity, porosity, and retardation coefficients (McTernan 1990).

Mathematical models offer the most promising method of assessing the waste disposal system. These models incorporate physicochemical characteristics of a landfill environment to predict solute movement. The models use a set of differential equations with boundary conditions to evaluate data obtained from a landfill site. Models are based on ideal conditions and are therefore limited in their ability to accurately emulate field conditions. Models presented will assume that the porous medium is homogeneous, that isotropic, saturated flow is steady state, and that Darcy's law applies. Because of these assumptions, mathematical models should be used in conjunction with data gathered from the natural environment to assess the transport of pollutants at a disposal site.

There are many limitations in modeling reactions occurring in the lithosphere. The theoretical concentration of chemical species in solution, at equilibrium with the solid phase, can be calculated by using the enthalpies and entropies of formation of the various components of the system. A problem with the application of equilibrium thermodynamics to mineral dissolution and precipitation is that kinetic

constraints may control the extent of mineral reactions even when the soil solution is supersaturated (Evans 1989). It is not unlikely that supersaturation could occur, perhaps as the result of kinetic barriers to crystallization of small particles (Lovering 1976). Kinetic limitations are not significant in modeling the transport of lead in the subsurface. Lead reaches sorptive equilibrium in approximately 48 hours (Davis 1991). Mechanistic models describing interactions between humic substances and metals are not available. This large scale structural characterization is not possible because of the large number of functional groups and geometric configurations (Avogadro 1993). Solvent movement through the subsurface is difficult to predict because of the heterogeneous environment. Faults, cracks, soil stratification, compaction, and other physical features that affect the movement of water are difficult to identify and model. Despite these limitations, models can provide useful information.

## Sorption Isotherms

The transport of metals through the geologic environment is normally affected by sorption to the solid aquifer material. Because of the difficulty of measuring different molecular sorption mechanisms at the soil-water interface, data is attained by measuring the sorbate concentration in solution before and after contact with the sorbent. The relationship between solute and sorbed concentration is termed a "sorption isotherm." The equilibrium state can be described by a linear isotherm (Equation 5). The distribution coefficient,  $K_d$ , is equal to the slope of the isotherm. This coefficient is only valid for chemical and physical conditions similar to the experiment.

$$K_d = \frac{\rho_b s}{\varepsilon C} = \frac{q}{C} \quad [\text{Eq 5}]$$

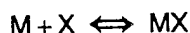
When sorption is stronger (higher  $K_d$ ), more retardation occurs. The use of the distribution coefficient assumes that partitioning reactions between solute and soil are very rapid relative to the velocity of the groundwater. Therefore, it is possible for nonequilibrium fronts to occur that appear to migrate faster than retarded fronts at equilibrium. The use of a retardation factor is presently a common option to model transport of pollutants (Appelo 1993). Equation 6 defines the retardation factor.

$$R = K_d + 1 \quad [\text{Eq 6}]$$

The retardation factor is equivalent to the ratio of the velocity of the sorbing contaminant to the velocity of the groundwater, and ranges from one to several thousand. The velocity of the contaminant with respect to water velocity can be calculated using Equation 7.

$$v_c = \frac{v}{R} \quad [\text{Eq 7}]$$

The simple linear relation is not accurate in all cases; a curved plot of sorbance versus solute concentration will often be more appropriate. The Freundlich and Langmuir isotherms are the most commonly used nonlinear isotherms (Appelo 1993). Lead sorbed to soil constituents, e.g., Fe/Mn/Al oxides, clays, and organic material, can generally be described using the Langmuir and Freundlich isotherms (Fergusson 1990). The simplest isotherm is that based on the equation proposed by Langmuir to describe the adsorption of a gas onto a planer surface. Its application to soils can be derived by writing the sorption reaction as:



A mass balance on all the sites results in Equation 8. The Langmuir equation describes a rectangular hyperbola with "max" being the asymptotic value of the hyperbola.

$$\Gamma = \frac{\Gamma_{\max} \cdot K_{\text{ads}} \cdot [C]}{1 + K_{\text{ads}} \cdot [C]} \quad [\text{Eq 8}]$$

The isotherm assumes that all sorption sites are equivalent, that bonding is reversible, and that metal ions do not interact with one another and form a single layer. In the natural environment, sorption sites are not all equivalent and there is interaction between metal ions. However, if the concentration of metal ions is low, the isotherm provides a good approximation of actual conditions. Typical heavy metal concentrations in groundwater are low; therefore, the isotherm is considered applicable.

The Freundlich isotherm is more general than the Langmuir because it allows for surface heterogeneity. At high concentrations, sorbed molecules typically arrange themselves in several layers (Avogadro 1993). The Freundlich isotherm (Equation 9) can be used to describe sorption of metals.

$$\log \Gamma = \log A + \frac{1}{n} \cdot \log [C] \quad [\text{Eq 9}]$$

A and n are constants obtained by fitting the isotherm to experimental data. The isotherm assumes that the affinity of the sorption sites decreases exponentially as sorption increases. When the sorbent approaches saturation, the isotherm is not longer applicable because the Freundlich, like the linear isotherm, indicates the surface concentration can increase indefinitely, which is not the case in nature.

Nonlinear equations commonly describe experimental data better than linear equations. This is largely due to the coefficients that can be manipulated to fit experimental data. Experimental data are often fitted to some linearized form of the equations presented in this paper. However, it has been shown that this results in biased results, and that a nonlinear, least-squares fit should be preferred (Appelo 1993).

## Transport

Breakthrough curves for different soils can be used to predict pollutant migration rates. A breakthrough curve is created for a soil/contaminate pair from experimental data. Characteristics of soils at locations of interest can be compared to tested soils to estimate their attenuation characteristics. Breakthrough curves are used to determine average velocities and dispersion coefficients. This requires a fit of experimental data with the analytical solution of a differential transport equation.

Equation 10 is commonly used to mathematically model one-dimensional transport in a porous medium. The equation takes into account diffusion, dispersion, and advective flow, but does not account for retardation. A solute that moves according to Equation 10 is defined as an ideal or conservative tracer.

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D_h \frac{\partial^2 C}{\partial x^2} \quad [\text{Eq 10}]$$

When a tracer is supplied continuously in a column that is initially tracer free, this equation can be used to describe its flow:

$$\begin{aligned} C(x=0, t>0) &= C_0 \\ C(x, t=0) &= 0 \end{aligned}$$

The solution for these boundary conditions for an infinite column is shown in:

$$C = 0.5C_0 \left[ \operatorname{erfc} \left( \frac{x-vt}{2\sqrt{D_h t}} \right) + \exp \left( \frac{xv}{D_h} \right) \operatorname{erfc} \left( \frac{x+vt}{2\sqrt{D_h t}} \right) \right] \quad [\text{Eq 11}]$$



The center of mass ( $C/C_o = 0.5$ ) of the breakthrough curve travels with the average linear velocity of the solvent.

Retardation slows the velocity at which reactive solutes travel through a medium. There are many reactions that retard the migration of nonconservative materials, but sorption appears to be the dominant mechanism (Bedient 1994). Therefore, retardation is modeled as if sorption were the only mechanism that affects the transport of a given pollutant. Equation 12 is used to describe both conservative and nonconservative transport mechanisms. Isotherms are used to relate the concentration of a contaminant sorbed, by a solid, to the amount in solution. This equation is very similar to Equation 10 because it is assumed that nonconservative mechanisms affect reactive contaminant in the same manner as tracers.

$$\frac{\delta C}{\delta t} = -v \frac{\delta C}{\delta x} + D_h \frac{\delta^2 C}{\delta x^2} - \frac{\delta q}{\delta t} \quad [\text{Eq 12}]$$

Using the same boundary conditions used to derive Equation 11 and the Freundlich isotherm, Equation 13 can be solved yielding the following equation:

$$C = 0.5C_o \left[ \text{erfc} \left( \frac{Rx - vt}{2\sqrt{RD_h t}} \right) + \exp \left( \frac{xv}{D_h} \right) \text{erfc} \left( \frac{Rx + vt}{2\sqrt{RD_h t}} \right) \right] \quad [\text{Eq 13}]$$

Large values of  $D_h$  tend to spread out the fronts, while large values of  $R$  tend to slow the velocity of the center of mass and reduce  $D_h$  by a factor of  $1/R$ . One-dimensional mathematical models are present above; more complicated models involving more dimensions often use computers. These models require more input that is not commonly available for most landfills because of the expense of collecting data. Two-dimensional models can be solved analytically for simple boundary conditions, but numerical models are generally required for actual field conditions (Bedient 1994). For more information on two and three-dimensional modeling see *Ground Water Contamination Transport and Remediation* (Bedient 1994).

## 7 Equipment and Materials

The laboratory experiment was designed using the following equipment and materials.

### Reagents

A	Calcium Montmorillonite	Ca-Montmorillonite Clay, Apache County, AZ CEC = 120 meq/100g, SA = 97.42 m <sup>2</sup> /g
B	Carbon Dioxide Gas	Laboratory Grade compressed CO <sub>2</sub> gas
C	Chromerge™	Chromerge™ Cleaning Solution, For preparing Chromic Sulfuric Acid Solution, mix 25 mL into 2.5 L of Concentrated Sulfuric Acid
D	Fulvic Acid	Material and characterization (page X) provided by: Professor R.F. Howe Department Head of Physical Chemistry, School of Chemistry, Univ. of New South Wales, Kensington, Australia
E	Hydrochloric Acid	37% HCl (12 Molar), Reagent Grade.
F	Kaolin	Kaolin Clay, Well-Crystallized, Washington County, GA. Cation Exchange Capacity (CEC) = 2.0 meq/100g, Surface Area (SA) = 10.05 m <sup>2</sup> /g
G	Lead Reference Solution	Lead Reference Standard Solution, Certified, Concentration = 1000 ppm ± 1% Pb, For Atomic Adsorption (1mL = 1 mg Pb), Solute: Lead Metal, Solution : Dilute Nitric Acid.
H	Lead (II) Chloride	99.999% PbCl <sub>2</sub> , Solubility at 20° C = 9.9 g/L, mp = 501° F, bp = 950° F
I	Milli-Q Water	Millipore Corporation, Milli-Q™ 4-bowl water treatment system Characteristics of effluent: •Total Dissolved Solids <0.03 ppm •Conductivity <0.056 µmhos/cm •Heavy Metals < 0.01 ppm •Organics < 50 ppb
J	Nitric Acid	68% to 71% HNO <sub>3</sub> W/W Trace Metal Grade
K	Nitrogen Gas	Laboratory Grade compressed N <sub>2</sub> gas
L	Oxygen Gas	Laboratory Grade compressed O <sub>2</sub> gas
M	pH 4 Buffer Solution	Fisher Scientific, Potassium Biphthalate Buffer certified ± 0.01 @ 25°C
N	pH 7 Buffer Solution	Fisher Scientific, Potassium Phosphate Monobasic-Sodium Hydroxide Buffer certified ± 0.01 @ 25°C
O	Phosphoric Acid	H <sub>3</sub> PO <sub>4</sub> , Volatile Acids (as Acetic) < 0.001% •Heavy Metals (as Pb) < 0.001% •Assay Minimum - 85%
P	Potassium Hydrogen Phthalate	HOCO <sub>6</sub> H <sub>4</sub> COOK, •Assay 100.04% •Heavy Metals (as Pb) < 1 ppm
Q	Potassium Persulfate	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , •Assay 100.3% •Heavy Metals (as Pb) < 0.0003%
R	Sulfuric Acid	96% H <sub>2</sub> SO <sub>4</sub> (18 Molar), Reagent Grade.

## Fulvic Acid Characterization

The fulvic acid was extracted from swamp water obtained from the Myall Lakes area of New South Wales, Australia. The average molecular weight was determined by gel permeation chromatography to be 14,245 (range 4,000 to 52,000). An IR spectrum was run as a KBr pellet at 4 cm<sup>-1</sup> resolution (Figure 3). An NMR was run at 300 MHz by CP/MAS (4,000 Hz spinning speed, 1 m sec contact time) (Figure 4).

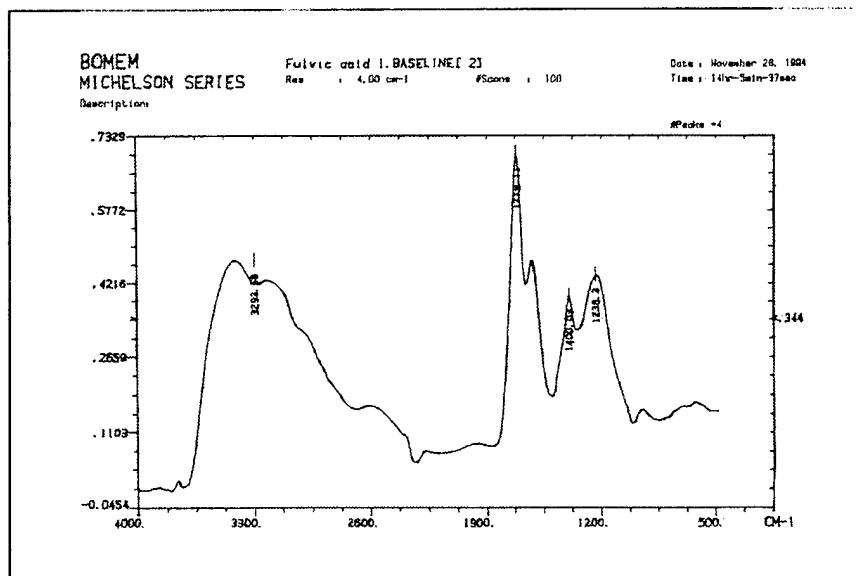


Figure 3. Fulvic acid IR spectrum.

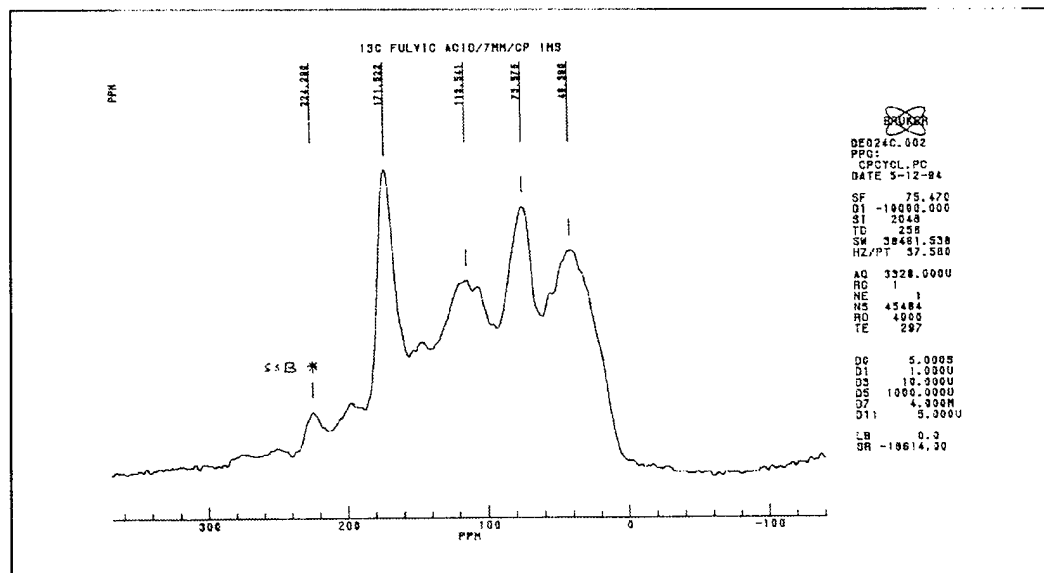


Figure 4. Fulvic acid NMR.

## Equipment

A	Atomic Absorption Spectrophotometer	Thermo Jarrel Ash Atomic Absorption Spectrophotometer Model Smith-Hieftje 11™; Specifications: <ul style="list-style-type: none"> <li>• Wavelength range = 180 to 900 nm</li> <li>• Bandpass = 0.04 to 2 nm</li> <li>• Scattered light &lt; 0.2%</li> <li>• Focal length = 1/3 meter</li> <li>• Light source: single element hollow cathode lamp</li> <li>• Fuel: acetylene</li> <li>• Sensitivity = 0.1 mg/L</li> </ul>
B	Automatic Dispenser	Fisher/Wheaton™ Adjustable-volume bottle-top dispensers; Specifications: <ul style="list-style-type: none"> <li>• Dispenses from 10 to 59 mL (in 1.0 mL increments)</li> <li>• Accuracy of ± 0.5% and reproducibility of ± 0.1%</li> <li>• 2.5 L amber bottle</li> </ul>
C	Automatic Pipetter	Oxford™ automatic pipetter; Specifications: <ul style="list-style-type: none"> <li>• Dispenses from 1.0 to 10.0 mL</li> <li>• Precision of ± 0.5%</li> <li>• Glass dispensing assembly with Teflon™ fluorocarbon resin connectors</li> <li>• 1.2L wide-mouth amber bottle</li> </ul>
D	Centrifuge	Sorvall® General Laboratory Centrifuge GLC-2; Specifications: <ul style="list-style-type: none"> <li>• HL-4 Horizontal Rotor</li> <li>• 50 mL Bucket</li> <li>• Maximum rotor speed = 3,200 rpm</li> <li>• Operating temperature = +4°C to +40°C</li> </ul>
E	CO <sub>2</sub> Gas Regulator	Fisher™ Carbon Dioxide single stage gas regulator
F	Conductivity Meter	Orion™ Model 124 Conductivity/TDS Meter; Specifications: <ul style="list-style-type: none"> <li>• Four electrode cell</li> <li>• Conductivity measurements with 0.5% accuracy to a maximum of 199,990 µS/cm</li> <li>• Compensates for temperature by using coefficient of 2.2% (readings corrected to 25°C)</li> <li>• Temperature readings from -5°C to +50°C (23°F to 122°F) with accuracy of ±0.1°C</li> <li>• TDS readings from 0 to 2000 ppm</li> <li>• LCD Display • Abrasion-proof electrode</li> </ul>
G	Gyrotory Shaker	New Brunswick Scientific Co., Inc. Digital Gyrotory Shaker Model G-10; Specifications: <ul style="list-style-type: none"> <li>• Orbital shaking with 1" diameter</li> <li>• Speed range from 40 to 400 rpm</li> <li>• LED rate indication</li> <li>• Continuous-duty, industrial-grade 1/8 hp motor</li> <li>• 24 x 36" universal platforms with 4" high side rails</li> </ul>

H	Magnetic Stirrer	Thermolyne Nuova II™ Magnetic Stirrer Model # S18525 Series 307; Specifications: <ul style="list-style-type: none"> <li>• 7" x 7" stirring surface</li> <li>• Speed range of 100 to 1000 rpm</li> <li>• Teflon™ fluorocarbon resin coated stir bar</li> </ul>
I	pH Meter	Corning Model 340 pH/ion Meter; Specifications: <ul style="list-style-type: none"> <li>• pH range of -2 to 16 with accuracy of <math>\pm 0.01</math></li> <li>• mV range of <math>\pm 1999</math> with accuracy of <math>\pm 1</math></li> <li>• 2 point calibration with auto buffer recognition</li> <li>• LCD Display</li> </ul>
J	pH Probe	Fisher™ gel-filled polymer body pH electrode; Specifications: <ul style="list-style-type: none"> <li>• pH range of 0 to 14</li> <li>• Temp. range of -5° to +80°C</li> <li>• Filled with gelled 4M KCl saturated with AgCl electrolyte</li> <li>• BNC Connector</li> </ul>
K	Scale	Mettler AE 200 Scale; Specifications: <ul style="list-style-type: none"> <li>• Measuring Range = 0 to 204.9999 g</li> <li>• Accuracy <math>\pm .0001</math>g</li> </ul>
L	TOC Analyzer	XERTEX Dohrmann® DC-80 Automated Laboratory Total Organic Carbon Analyzer; Specifications: <ul style="list-style-type: none"> <li>• Operating modes: total, organic, &amp; inorganic carbon</li> <li>• Method: ultra-violet promoted chemical oxidation, infra-red detection</li> <li>• Repeatability = <math>\pm 2\%</math></li> <li>• Detector: linearized non-dispersive infra-red</li> <li>• Range: 0.1 to 800 mg/L</li> </ul>

## Materials

A	Acid Bath Containers	Nalgene heavy-duty HDPE tanks and covers (18"L x 12"W x 12"H)
B	Centrifuge Tubes	PYREX® 50 mL (#8422) glass centrifuge bottles with GPI threaded 24-410 screw caps
C	Electrode Reservoir	Fisher electrode reservoir <ul style="list-style-type: none"> <li>• Threaded polyethylene bottle with punched cap and O-ring seal</li> </ul>
D	Isotherm Bottles	I-Chem™ 250 mL clear flint glass wide-mouth bottles with teflon-lined closures.
E	Pb Standard Bottles	Nalgene high-density polyethylene(HDPE) fluorinated bottles and HDPE screw closures.
F	Sample Bottles	Qorpak™ 50 mL clear flint glass wide-mouth bottles with Teflon™ TFE fluorocarbon resin lined closures.
G	Syringe	Micro-Mate® Interchangeable Hypodermic Syringe, 50cc Luer Needle Lock

H	Syringe Filters	MSI™ Cameo 25ES Syringe Filters; Specifications: <ul style="list-style-type: none"><li>• 25mm filter</li><li>• Biologically inert, hydrophilic MicronSep nitrocellulose</li><li>• Modified acrylic housing</li><li>• Individually packaged</li><li>• Gamma radiation sterilized</li></ul>
I	Volumetric Flasks	10 mL, 25 mL, 50 mL, 100 mL, 500 mL, 1000 mL, 2000 mL Kimax™ Volumetric Flasks with standard taper stopper
J	Wash Bottles	Nalgene™ 250 mL low-density polyethylene unitary wash bottles with polypropylene screw closures

## Stock Solutions

### ***1250 ppm Lead Solution.***

1. Weigh out 1.6778 g of  $\text{PbCl}_2$ .
2. Place the material in a 1000 mL volumetric flask.
3. Add 3 drops of HCl.
4. Dissolve the  $\text{PbCl}_2$  in deionized water to make a 1000 mL stock solution.
5. Dispense 1 mL of the stock solution into a 1000 mL volumetric solution.
6. Add deionized water to make a 1000 mL solution.
7. Verify that the solution has 4 ppm lead using atomic adsorption.
8. Pour stock solution into an automatic pipetter.

### ***1250 ppm Fulvic Acid Solution.***

1. Weigh out 1.250 grams of fulvic acid.
2. Place material in 1000 mL volumetric flask.
3. Add deionized water to make a 1000 mL solution.

The graph shown in Figure 5 was used to convert fulvic acid mass to TOC. Four dilutions were made from a solution containing a known mass of fulvic acid. The TOC of each dilution was determined using the total organic carbon analyzer.

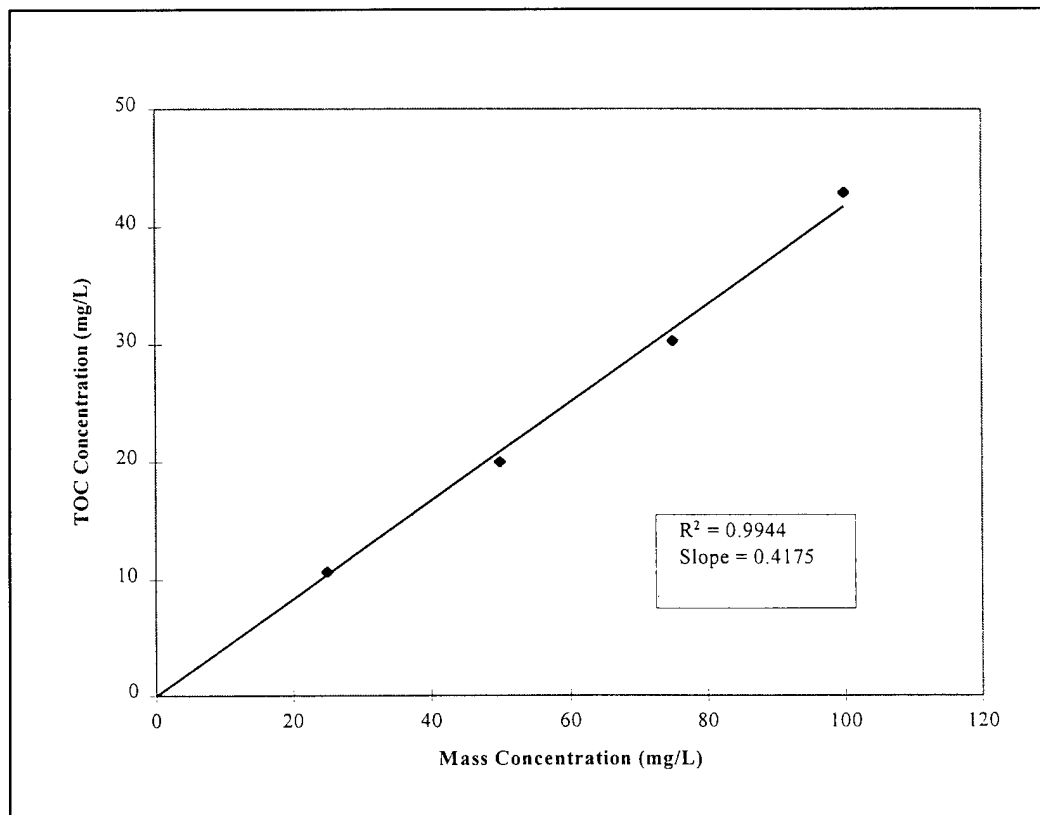


Figure 5. Fulvic acid mass vs. TOC concentrations.

## 8 Methods

The following methods were used to determine experimental parameters.

### Determination of the Soil:Solution Ratio

1. Weigh out the clay into each isotherm bottle.

Bottle	Clay (g)
1	10
2	5
3	2
4	1
5	0.4
6	0
7	2

2. Dispense deionized water into each isotherm bottle so they each contain 200 mL of solution minus the volume of lead to be added.
3. Bubble CO<sub>2</sub> through the solution contained in each isotherm bottle being careful not to lose solution.
4. Place isotherm bottles on shaker table for 24 hours.
5. Open bottle and purge headspace continually with CO<sub>2</sub>.
6. Dispense 20 mL of lead solution into each isotherm bottle except bottle seven.
7. Measure the initial conductivity of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
8. Measure the initial pH of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
9. Shut off CO<sub>2</sub> and cap the isotherm bottles.
10. Place isotherm bottles vertically on shaker table for 48 hours at 250 rpm.
11. Remove isotherm bottles from shaker table.
12. Measure the final pH of the solution in each of the sample bottles using a probe. Rinse probe between each reading.



13. Measure the final conductivity of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
14. Pour the supernate of each isotherm bottle into a centrifuge tube, purge head space with CO<sub>2</sub> and cap.
15. Centrifuge the solution at 3,200 rpm for 30 minutes.
16. Place a 0.45µm filter on the outlet of the syringe.
17. Pour the supernate into a syringe, and dispense approximately 5 mL into a waste container.
18. Dispense the remaining supernate into a 50 mL sample bottle.
19. Dispose of the 0.45µm filter.
20. Dispense 2 drops of HCl into each 50 mL sample bottles.
21. Determine the concentration of lead in solution using atomic adsorption.

### Determination of Equilibration Time

1. Weigh out clay and place in isotherm.

Clay Material	Soil:Solution Ratio	Mass of Clay (g)
Kaolinite	1:50	4
Montmorillonite	1:200	1

2. Dispense deionized water into each isotherm bottle so they each contain 200 mL of solution minus the volume of lead to be added.
3. Bubble CO<sub>2</sub> through the solution contained in each isotherm bottle being careful not to lose solution.
4. Place isotherm bottles on shaker table for 24 hours.
5. Open bottle and purge headspace continually with CO<sub>2</sub>.
6. Dispense 20 mL of lead solution into each isotherm bottle except bottle seven.
7. Measure the initial conductivity of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
8. Measure the initial pH of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
9. Shut off CO<sub>2</sub> and cap the isotherm bottles.
10. Place isotherm bottles vertically on shaker table at 250 rpm.
11. Remove each isotherm bottle from shaker table after the specified time has elapsed.

Bottle	Clay Solution (mL)	Time (hours)
1	50	1
2	50	24
3	50	48
4	50	72
5	0	72

12. Measure the final pH of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
13. Measure the final conductivity of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
14. Pour the supernate into a centrifuge tube, purge head space with CO<sub>2</sub> and cap.
15. Centrifuge the solution at 3,200 rpm for 30 minutes.
16. Place a 0.45µm filter on the outlet of the syringe.
17. Pour the supernate into a syringe, and dispense approximately 5 mL into a waste container.
18. Dispense the remaining supernate into a 50 mL sample bottle.
19. Dispose of the 0.45µm filter.
20. Dispense 2 drops of HCl into each 50 mL sample bottles.
21. Determine the concentration of lead in solution using atomic adsorption.
22. Repeat steps 9 through 20 for each isotherm bottle.

### Clay-Lead Isotherms

1. Weigh out clay and place in each isotherm bottle, except bottle 10 which should contain no clay material.

Clay Material	Soil:Solution Ratio	Mass of Clay (g)
Kaolinite	1:50	4
Montmorillonite	1:200	1

2. Dispense deionized water into each isotherm bottle so they each contain 200 mL of solution minus the volume of lead to be added.
3. Bubble CO<sub>2</sub> through the solution contained in each isotherm bottle being careful not to lose solution.
4. Place isotherm bottles on shaker table for 24 hours.
5. Open bottle and purge headspace continually with CO<sub>2</sub>.
6. Dispense the lead solution into each isotherm bottle.

7. Measure the initial conductivity of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
8. Measure the initial pH of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
9. Shut off CO<sub>2</sub> and cap the isotherm bottles.
10. Place isotherm bottles vertically on shaker table for 48 hours at 250 rpm.
11. Remove isotherm bottles from shaker table.
12. Measure the final pH of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
13. Measure the final conductivity of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
14. Pour the supernate of each isotherm bottle into a centrifuge tube, purge head space with CO<sub>2</sub> and cap.
15. Centrifuge the solution at 3,200 rpm for 30 minutes.
16. Place a 0.45µm filter on the outlet of the syringe.
17. Pour the supernate into a syringe, and dispense approximately 5 mL into a waste container.
18. Dispense the remaining supernate into a 50 mL sample bottle.
19. Dispose of the 0.45µm filter.
20. Dispense 2 drops of HCl into each 50 mL sample bottles.
21. Determine the concentration of lead in solution using atomic adsorption.

### Clay-Fulvic Acid Isotherms

1. Weigh out clay and place in each isotherm bottle, except bottle 10, which should contain no clay material.

Clay Material	Soil:Solution Ratio	Mass of Clay (g)
Kaolinite	1:50	4
Montmorillonite	1:100	2

2. Dispense deionized water into each isotherm bottle so they each contain 200 mL of solution minus the volume of fulvic acid to be added.
3. Bubble CO<sub>2</sub> through the solution contained in each isotherm bottle being careful not to lose solution.
4. Place isotherm bottles on shaker table for 24 hours.
5. Open bottle and purge headspace continually with CO<sub>2</sub>.
6. Dispense the fulvic acid solution into each bottle.
7. Measure the initial conductivity of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.

8. Measure the initial pH of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
9. Shut off CO<sub>2</sub> and cap the isotherm bottles.
10. Place isotherm bottles on shaker table for 72 hours at 250 rpm.
11. Remove isotherm bottles from shaker table.
12. Measure the final pH of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
13. Measure the final conductivity of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
14. Pour the supernate of each isotherm bottle into a centrifuge tube, purge head space with CO<sub>2</sub> and cap.
15. Centrifuge the solution at 3,200 rpm for 30 minutes.
16. Place a 0.45µm filter on the outlet of the syringe.
17. Pour the supernate into a syringe, and dispense approximately 5 mL into a waste container.
18. Dispense the remaining supernate into a 50 mL sample bottle.
19. Dispose of the 0.45µm filter.
20. Place 2 drops of concentrated phosphoric acid in each sample.
21. Purge sample with nitrogen for approximately 5 minutes.
22. Determine the concentration of fulvic acid in solution using TOC analyzer.

### Clay-Lead-Fulvic Acid Isotherms

1. Weigh out clay and place in each isotherm bottle, except bottle 10 which should contain no clay material.

Clay Material	Soil:Solution Ratio	Mass of Clay (g)
Kaolinite	1:50	4
Montmorillonite	1:200	1

2. Dispense deionized water into each isotherm bottle so they each contain 200 mL of solution minus the volume of fulvic acid to be added.
3. Bubble CO<sub>2</sub> through the solution contained in each isotherm bottle being careful not to lose solution.
4. Place isotherm bottles on shaker table for 24 hours.
5. Open bottle and purge headspace continually with CO<sub>2</sub>.
6. Dispense the fulvic acid solution into each bottle.
7. Dispense the lead solution into each isotherm bottle.
8. Measure the initial conductivity of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.

9. Measure the initial pH of the solution in each of the isotherm bottles using a probe. Rinse probe between each reading.
10. Shut off CO<sub>2</sub> and cap the isotherm bottles.
11. Place isotherm bottles on shaker table for 72 hours at 250 rpm.
12. Remove isotherm bottles from shaker table.
13. Measure the final pH of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
14. Measure the final conductivity of the solution in each of the sample bottles using a probe. Rinse probe between each reading.
15. Pour the supernate of each isotherm bottle into a centrifuge tube, purge head space with CO<sub>2</sub> and cap.
16. Centrifuge the solution at 3,200 rpm for 30 minutes.
17. Place a 0.45µm filter on the outlet of the syringe.
18. Pour the supernate into a syringe, and dispense approximately 5 mL into a waste container.
19. Dispense the remaining supernate evenly into two 50 mL sample bottles.
20. Dispose of the 0.45µm filter.
21. Dispense 2 drops of HCl into one 50 mL sample bottles to be used for lead analysis.
22. Determine the concentration of lead in solution using atomic adsorption.
23. Purge the second sample with nitrogen for approximately 5 minutes.
24. Determine the concentration of fulvic acid in solution using TOC analyzer.

## 9 Quality Control

The following quality control measures were taken to ensure consistent, reliable results.

### Cleaning of Equipment

#### *Glassware*

1. Soak glassware in chromic acid bath for 24 hours.
2. Drain and place glass in dilute chromic acid bath for 24 hours.
3. Rinse with deionized water.
4. Store bottles full of deionized water.

#### *Plastic lids*

1. Soak in dilute chromic acid bath for 24 hours.
2. Rinse with deionized water.
3. Store on bottles full of deionized water.

#### *Syringe*

1. Soak syringe in dilute chromic acid bath for 24 hours.
2. Rinse with deionized water.
3. Filter sample with the lowest concentrations of lead.
4. Soak in chromic acid solution for 20 minutes.
5. Rinse with deionized water.
6. Repeat step 3 through 5 until all the samples have been filtered.

#### *pH probe*

1. Rinse with deionized water between each use.
2. Store in pH 7 buffer solution.

### ***Carbon Dioxide Dispenser and EC probe***

Rinse with deionized water between each use.

## **Operation and Calibration of Equipment**

### ***pH Probe***

1. Calibrate probe using pH buffers 4.00 and 7.00 in accordance with manual supplied by the manufacturer.
2. Measure solutions from least concentrated to most concentrated rinsing probe between each reading.
3. Check probe accuracy using pH 4 standard after every 10 readings.

### ***Atomic Adsorption***

#### **Standards**

1. Dispense calculated lead reference volume into 200 mL volumetric flasks.
2. Add deionized water to make a 200 mL standard solution.

Standard Concentration	Volume of Lead Reference (mL)
2 ppm	0.4
4 ppm	0.8
6 ppm	1.2
8 ppm	1.6
10 ppm	2.0

3. Store solutions in Pb Standard Bottles.

#### **Sample Dilution**

1. If lead concentration in sample exceeds 10 ppm, dilution is required.
2. Deionized dilution water is acidified with 2 drops of HCl per 50 mL, before sample is added.

#### **Operation**

1. See the manual supplied by the manufacturer for operation of the equipment.
2. Operate machine at wavelength = 217 nm, bandpass = 1.0 nm, and lamp current = 5.0 ma.

3. Operate the burner at long path and have an oxidizing, fuel lean, blue flame.
4. Generate standard curve using 2, 4, 6, 8 and 10 ppm lead reference solutions.
5. All samples are analyzed twice and the average value is reported.
6. Check readings every 10 samples with a reference solution.
7. If the machine has drifted more than 0.05 ppm, rezero and autocalibrate the atomic adsorption unit.
8. Read the last 10 samples again.
9. Store reference solutions at 20 °C in plastic bottles.

### ***TOC analyzer***

#### **Potassium Persulfate Reagent**

1. Weigh out 20 g potassium persulfate
2. Place the material in a 1000 mL volumetric flask.
3. Add 1 mL of concentrated phosphoric acid.
4. Dissolve the solution in deionized water to make a 1000 mL stock solution.
5. Store in cool, dark place
6. Replace monthly

#### **Organic Carbon Standard**

1. Weigh out 425 mg of potassium hydrogen phthalate
2. Place the material in a 1000 mL volumetric flask.
3. Add 0.1 mL of concentrated phosphoric acid.
4. Dissolve the solution in deionized water to make a 1000 mL 2000 ppm carbon stock solution.
5. Dilute the stock solution to make 400 ppm carbon standard
6. Store in cool, dark place
7. Replace monthly

#### **Operation**

1. See the manual supplied by the manufacturer for operation of the equipment.
2. Use three injections 400 ppm C standard to calibrate the instrument.
3. Standard reading should not deviate by more than 2 percent.
4. All sample are read 3 times and the average is reported.
5. Every 20 samples verify the calibration of the instrument by injecting the 400 ppm C standard.
6. Recalibrate the machine if the reading deviates by more than 8 ppm C.



***Stock Solution Dispensers***

1. Calibrate dispensers using volumetric flasks.
2. Check accuracy every 20 dispenses.

## 10 Analysis

### Materials

#### *Clay*

Kaolinite and calcium montmorillonite samples were tested for leachable lead and organics. The samples were placed in isotherm bottles with deionized water for 24 hours and mixed. A pH of approximately 4.3 was measured for samples containing kaolinite. The pH of the calcium montmorillonite samples was approximately 5.2. Detectable concentrations of lead and organic carbon were not measured in the supernatant. It would be incorrect however, to assume that the materials did not possess these constituents. The only conclusion that can be drawn is that the clay materials do not possess leachable quantities of lead and organic matter.

#### *Fulvic Acid*

Several fulvic acid samples were analyzed for lead. The samples were placed in isotherm bottles with deionized water for 24 hours and mixed. The samples were analyzed for lead using atom adsorption. No detectable concentrations of lead were found in the samples. Tests for other metals were not conducted.

The solubility of fulvic acid was tested to ensure that the material would not be removed while being centrifuged or filtered. Fulvic acid samples were analyzed to determine their initial total organic carbon concentrations. The samples were then placed in centrifuge bottles and centrifuged. A pH of 3.4 was typically measured in solutions containing only fulvic acid and deionized water. The supernatant was then filtered and analyzed for TOC. No detectable change was observed between the initial and final readings. It can be concluded that filtration and centrifugation do not remove fulvic acid from solution.

#### *Lead*

The solubility of  $PbCl_2$  was tested to ensure that the material would not be removed while being centrifuged or filtered. Lead samples were analyzed to determine their initial concentrations. The samples were then placed in centrifuge bottles and

centrifuged. The supernatant was then filtered and analyzed for lead. No detectable change was observed between the initial and final readings. The conclusion from this experiment is that lead is soluble and is not adsorbed onto the filter or glassware significantly. The measured pH of a solution containing only  $\text{PbCl}_2$  and deionized water was observed to be approximately 3.6. The organic content of the  $\text{PbCl}_2$  was not tested because the material was 99.999 percent pure.

## Equipment

### *AA Analyzer*

For all tests performed, at least two blanks containing only lead and deionized water were analyzed. The blanks were handled in the same manner as the other samples. The concentration of the blanks correlated to the highest and middle lead concentrations being tested. These blanks were analyzed to determine if precipitation was occurring. Precipitation of lead was suspected if the blanks deviated from the known initial lead concentration by more than 5 percent. Lead precipitation was not observed in any of the blanks tested.

### *TOC Analyzer*

For all tests performed containing fulvic acid, at least two blanks were analyzed. The blanks contained only fulvic acid and deionized water. The blanks were handled in the same manner as the other samples. Fulvic acid concentrations of 100 mg/L and 200 mg/L were used to prepare the blanks. The data obtained from the blanks was used to linearly adjust the data obtained from the TOC analyzer. The blanks were all within 5 percent of the correlation: 100.0 mg FA/L is equivalent to 41.8 mg TOC/L.

## Soil:Solution Ratio

The soil:solution ratio refers to the ratio of the mass of the adsorbent to the volume of the liquid. To develop a sorption isotherm, a soil:solution ratio must be used that permits enough solute to be sorbed to produce a measurable, statistically significant difference in solution concentration (Roy, 1991). The recommendation of 10 to 30 percent sorption for the highest concentration was used to get a rough estimate of the appropriate ratio. Kaolinite and calcium montmorillonite were tested using lead and fulvic acid separately to determine the appropriate soil:solution ratio for each test. A soil:solution ratio of 1:50 was used for all experiments involving kaolinite.

Calcium montmorillonite has a higher cation exchange capacity, so a soil:solution ratio for experiments involving lead was set at 1:200. For those experiments involving fulvic acid a soil:solution ratio was set at 1:100. The higher ratio was intended to make TOC analysis easier by creating a larger difference between initial and final concentrations.

## Equilibration Time

The repeatability of the experiments depends on the establishment of chemical equilibrium. The equilibration time was determined for kaolinite and montmorillonite reacting with lead and fulvic acid. The EPA suggests that the equilibration time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution equal to or less than 5 percent per 24-hour interval (Roy, 1991). The lead reaction with clay occurs rapidly; 24 hours is sufficient to reach equilibrium. To ensure equilibrium was reached, test involving only lead were run for 48 hours. Experiments involving fulvic acid required 72 hours to reach equilibrium. The times reported vary  $\pm 2$  hours because of the time required to remove and analyze each sample. Much of the data collected in 48 hours was verified by running duplicate tests for 72 hours to confirm equilibrium had been established. The results of the tests run for 48 and 72 hours were not statistically different, and the data collected from the verification data along with the original data were used to develop the isotherms presented in this document.

## Data Collection

All experiments were repeated to ensure that equilibrium had been reached and the results could be duplicated. Suspect data was retested to ensure that it was truly an outlier before being removed from the database. To ensure equilibrium had been reached, many of the repeated tests were run for 72 hours as opposed to 48 hours. Data points obtained from the repeated experiments are included in the database used to develop the isotherms. Experiments were performed at room temperature ( $22 \pm 3$  °C).

## Data Analysis

Freundlich and Langmuir Equations were used to fit the data collected. Consistently the Langmuir Equation fit the data much better. This was determined by calculating the  $r^2$  value for each equation and by visual inspection. The

Langmuir Equation was used to develop all isotherms presented in this document. The y-axis is the ratio of solute sorbed (x) to the mass of sorbent (m). The axis units are milligrams of lead or fulvic acid sorbed per gram of clay. The ratio is calculated using Equation 14.

$$\frac{x}{m} = \frac{(C_0 - C_f) \times \text{Solution} \cdot \text{Volume}}{\text{Clay} \cdot \text{Weight}} \quad [\text{Eq 14}]$$

All experiments performed used a solution volume of 0.2 L. The clay weight was measured in grams and depends on the soil:solution ratio. The x-axis is the measured concentration of lead or fulvic acid in milligrams/liter after filtration ( $C_f$ ). The data was linearized and a regression applied to obtain the constants for the Langmuir Equation. Isotherms were then plotted using the constants. The isotherms appear as solid black lines in Figures 6 to 9.

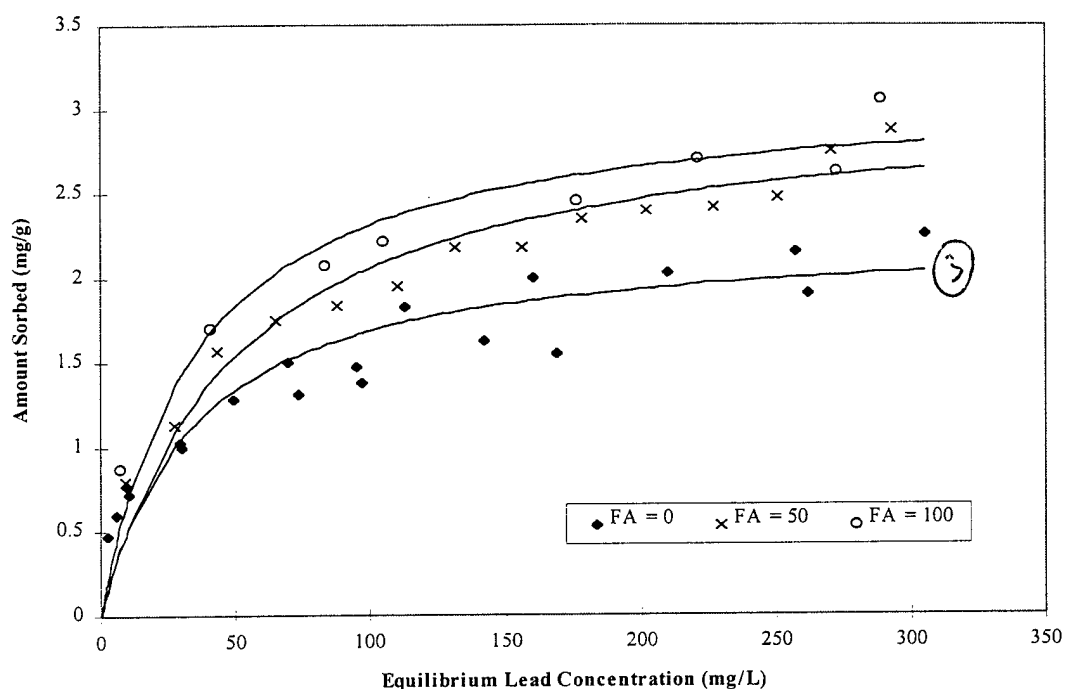
Electric conductivity ( $\mu\text{S}/\text{cm}$ ) and pH values are presented beneath each set of isotherms. The maximum, minimum, and average values for each data set, used to generate an isotherm, are reported. The range of pH and EC values measured are required for the correct interpretation of the data. This is because pH and EC are important parameters that affect the movement of lead in the subsurface. The initial (time = 0) and final (equilibrium) values are denoted by a subscript i or f, respectively in the first column. The initial and final values are provided to show the changes that occurred as the solutions equilibrated. The data provided also shows the effect of adding known amounts of lead or fulvic acid to a solution. In general, adding additional lead or fulvic acid increased the EC and decreased the pH in both the initial and final readings. A brief explanation of the collected data and observations is provided at the bottom of each page containing a set of isotherms and data.

A precipitant was observed in isotherm bottles containing only deionized water, fulvic acid, and lead. The reader should be aware that the sorption isotherms developed for mixed solutions containing lead and fulvic acid may be influenced by precipitation. It was assumed that precipitation played a minor role in the removal of lead from solution. The implications of the precipitant are presented in the discussion along with justification for the above assumption.

## Kaolinite Sorption Isotherms

### Lead

Lead sorption on kaolinite (Figure 6) agrees well with the clay's cation exchange capacity of 2 meq/100g. The introduction of 50 ppm fulvic acid to the solution increases the sorption of lead by approximately 36 percent. When 100 ppm fulvic acid was added, the sorption of lead increase roughly 39 percent. A 3 percent increase in lead sorption with a doubling of fulvic acid concentration indicates that the sites available for sorption were becoming saturated. Hypothetically, with increasing concentrations of fulvic acid, the sorption capacity for lead will approach a constant. The decrease in electric conductivity (EC) in all the tests reinforces the theory that lead and fulvic acid are being sorbed on the kaolinite. The average pH



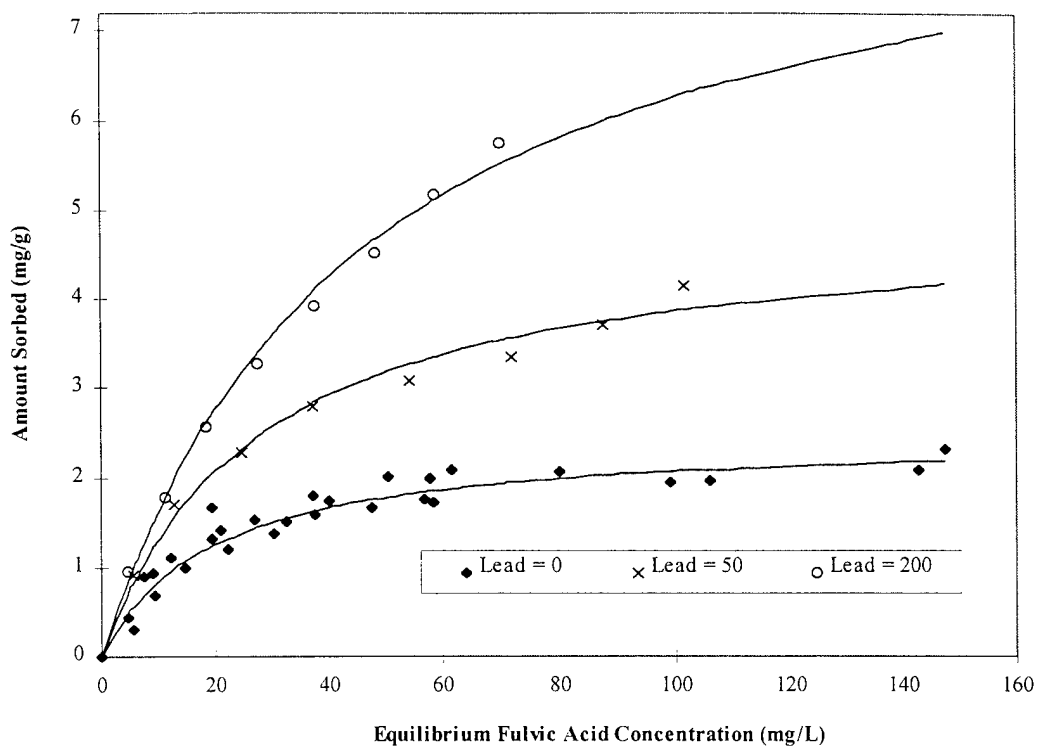
TEST	Max. pH	Min. pH	Avg. pH	Max. EC	Min. EC	Avg. EC	R <sup>2</sup>
(FA = 0) <sub>i</sub>	4.19	3.66	3.86	513	43	210	.96
(FA = 0) <sub>f</sub>	4.10	3.65	3.85	507	46	208	
(FA = 50) <sub>i</sub>	3.71	3.31	3.50	510	85	301	.98
(FA = 50) <sub>f</sub>	3.78	3.36	3.52	498	75	291	
(FA = 100) <sub>i</sub>	3.49	3.12	3.27	605	130	380	.98
(FA = 100) <sub>f</sub>	3.53	3.12	3.27	587	113	366	

Figure 6. Sorption of lead on kaolinite.

remained fairly constant during each experiment. It was observed that the pH of the solutions decreases as fulvic acid is added and EC increases.

### Fulvic Acid

The addition of 50 ppm PbCl<sub>2</sub> doubles the sorption of fulvic acid on kaolinite (Figure 7). A 270 percent increase in the sorption of fulvic acid is realized with the addition of 200 ppm PbCl<sub>2</sub>. This disproportional increase can be described using the same theory applied to the lead sorption on kaolinite in the presence of fulvic acid. The sorption sites are becoming saturated; as the PbCl<sub>2</sub> concentration increases, the sorption of fulvic acid will approach a constant value. A slight increase in the pH is observed during each test, indicating that fulvic acid is being taken out of solution. EC decreases in each test also indicating that lead and fulvic acid are being removed from solution. It was observed that, as PbCl<sub>2</sub> was added to the



TEST	Max. pH	Min. pH	Avg. pH	Max. EC	Min. EC	Avg. EC	R <sup>2</sup>
(Pb = 0) <sub>i</sub>	4.09	3.70	3.70	129	30	65	.97
(Pb = 0) <sub>f</sub>	4.19	3.87	3.87	103	30	53	
(Pb = 50) <sub>i</sub>	3.62	3.38	3.38	229	110	171	.98
(Pb = 50) <sub>f</sub>	3.87	3.54	3.54	210	103	152	
(Pb = 200) <sub>i</sub>	3.56	3.29	3.29	422	296	364	.97
(Pb = 200) <sub>f</sub>	3.65	3.37	3.37	412	290	354	

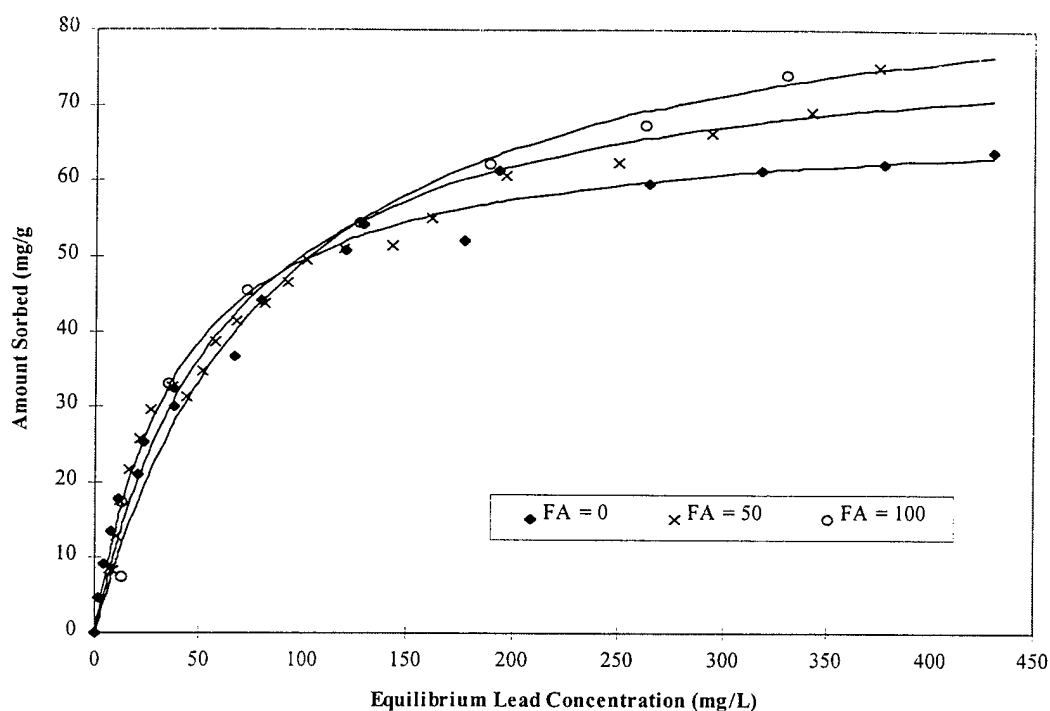
Figure 8. Sorption of fulvic acid on kaolinite.

solution the pH dropped. This may be attributed to lead displacing protons from sorption sites.

## Calcium Montmorillonite Sorption Isotherms

### Lead

Lead sorption on calcium montmorillonite, Figure 8, is approximately half of the clay's cation exchange capacity. Competition for sorption sites from calcium ions or depressed pH may be responsible for this observation. At low lead concentrations there is no statistical affect of fulvic acid on apparent lead sorption. At high concentrations the same trend develops that was observed with kaolinite. With increasing fulvic acid concentrations, there is increased sorption of lead. The data indicates



TEST	Max. pH	Min. pH	Avg. pH	Max. EC	Min. EC	Avg. EC	R <sup>2</sup>
(FA = 0) <sub>i</sub>	5.06	4.09	4.62	955	82	439	.99
(FA = 0) <sub>f</sub>	4.77	4.15	4.48	946	87	438	
(FA = 50) <sub>i</sub>	4.65	3.55	4.12	908	94	395	.99
(FA = 50) <sub>f</sub>	4.65	3.96	3.34	868	103	390	
(FA = 100) <sub>i</sub>	4.20	3.45	3.76	852	102	459	.95
(FA = 100) <sub>f</sub>	4.48	3.89	4.14	805	107	438	

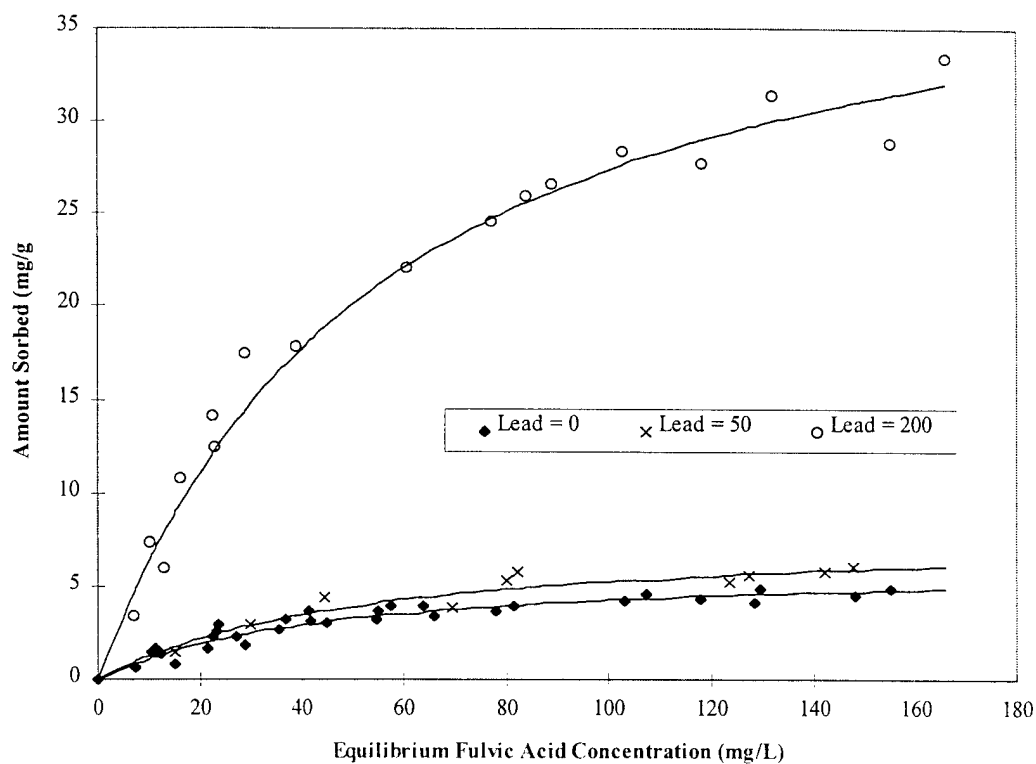
Figure 9. Sorption of lead on montmorillonite.



that, with increasing fulvic acid concentrations, a constant sorption capacity will be reached. The data correlates well with the Langmuir Equation. The EC decreased during each test indicating that the lead and fulvic acid were being removed from solution. The small decrease (< 5 percent) supports the theory that calcium ions are being displaced into solution.

### Fulvic Acid

It was observed that the ratio of fulvic acid sorbed (6.2:2.5) was much less than the ratio of the CEC (120:2) of calcium montmorillonite and kaolinite. This may be attributed to fulvic acid's inability to effectively displace the calcium ions from sorption sites. With the addition of lead the sorption increased slightly, but it was not until 200 ppm lead was introduced to solution that a significant increase in sorption was observed (Figure 9). High lead concentration gradients may be



TEST	Max. pH	Min. pH	Avg. pH	Max. EC	Min. EC	Avg. EC	R <sup>2</sup>
(Pb = 0) <sub>i</sub>	5.15	4.44	4.81	82	55	68	.91
(Pb = 0) <sub>f</sub>	5.18	4.55	4.92	91	72	81	
(Pb = 50) <sub>i</sub>	4.58	3.85	4.14	130	96	112	.92
(Pb = 50) <sub>f</sub>	4.41	4.04	4.23	123	107	113	
(Pb = 200) <sub>i</sub>	4.6	3.23	3.77	402	263	320	.95
(Pb = 200) <sub>f</sub>	4.83	3.47	4.07	339	267	294	

Figure 10. Sorption of fulvic acid on montmorillonite.

required to displace calcium from exchange sites. The pH of the solutions decreased as  $\text{PbCl}_2$  was added. This may once again be the result of protons being displaced into solution. During each test, the pH increased, indicating that fulvic acid was being removed from solution. No conclusive information can be obtained from the EC data except that calcium ions were being released as lead and fulvic acid were being sorbed.

## 11 Results

The disposal of lead-based paint has the potential to contaminate water supplies and geological formations if it is not managed properly. Information on the chemical fate of lead in the environment is necessary to minimize future financial, legal, and human health liabilities. The objective of this study was to investigate parameters that affect the movement of lead in disposal environments. Fulvic acid was chosen as a likely variable that would decrease attenuation of lead in the subsurface. Past research indicated that fulvic acid increases the solubility of lead, and was correlated with increased lead concentrations in leachate. This is first known study on the role of fulvic acid on lead mobility in the subsurface.

Fulvic acid is the product of biological decomposition and would likely be found in high concentrations in leachate. The initial hypothesis of this research was that fulvic acid would decrease the attenuation of lead in the subsurface. The hypothesis was incorrect and the following discussion will investigate the results, proposed chemical reactions that may explain what was observed, and the implications of this research on the field of waste disposal.

Lead sorption onto kaolinite was equal to the clay's cation exchange capacity. However, competition with calcium ions or the depressed pH of the solution prevented lead ions from occupying all the sorption sites on calcium montmorillonite. It was observed that the sorption of lead on clay materials was enhanced by the presence of fulvic acid. As the concentration of fulvic acid increased, the sorption of lead increased on both clay materials. The increased sorption was not proportional to the increase in fulvic acid (Table 11). The evidence suggests that as the fulvic acid concentration increases, the sorption of lead will approach a constant value.

Fulvic acid was able to occupy more of the available sorption sites on kaolinite than on calcium montmorillonite. The data collected supports the theory that fulvic acid molecules are not able to effectively displace multivalent

**Table 11. Langmuir constants (lead sorption).**

FA Conc. (mg/L)	$\Gamma_{\max}$ (mg/L)	$K_{\text{ads}}$
<i>Kaolinite</i>		
0	2.26	0.029
50	3.08	0.020
100	3.13	0.028
<i>Montmorillonite</i>		
0	68.67	0.026
50	80.68	0.017
100	92.04	0.012

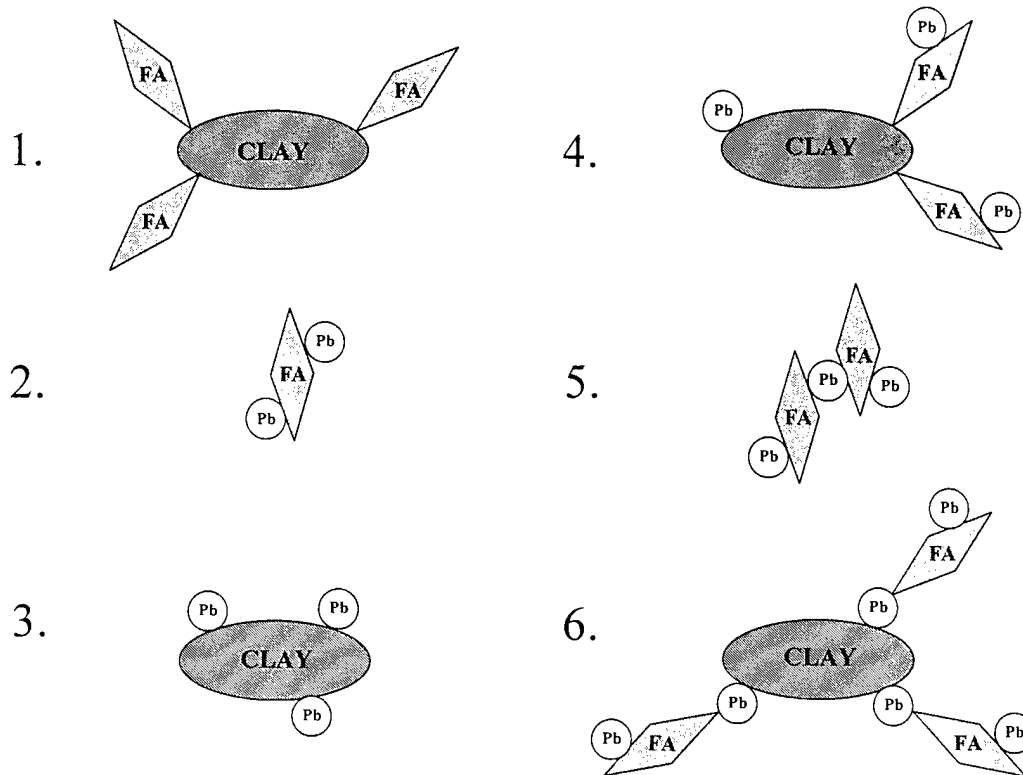
cations, such as calcium, from sorption sites. This observation is further support by information found in the literature. Fulvic acid sorption to clay materials was enhanced by increasing concentrations of lead in solution. The increased sorption was not proportional to the increase in lead (Table 12). The evidence suggests that, as the lead concentration increases, the sorption of fulvic acid will also approach a constant value.

**Table 12. Langmuir constants (fulvic acid sorption).**

Lead Conc. (mg/L)	$\Gamma_{\max}$ (mg/L)	$K_{\text{ads}}$
<i>Kaolinite</i>		
50	4.96	0.036
200	9.21	0.021
<i>Montmorillonite</i>		
0	6.20	0.022
50	8.09	0.019
200	43.08	0.017

Precipitation of a lead-fulvic acid complex was observed in bottles not containing clay. The complex stayed in suspension, but could be removed with centrifugation and filtration. The average EC of solutions containing lead, fulvic acid, and clay did not change more than 5 percent during equilibration. This observation supports the theory that sorption was the primary mechanism removing lead from solution. The ions removed from solution were replaced with ions displaced from sorption sites on the clay, keeping the EC relatively constant. If precipitation had been a significant removal mechanism, the EC would have dramatically decreased. A quantitative evaluation of the precipitation that occurred could not be obtained. The equilibrium thermodynamics of the reactions would need to be evaluated to determine the effect of precipitation on the apparent sorption. The formation of the complex would increase the attenuation of lead along with sorption on clay materials. The formation of a precipitant does not change the conclusion of this study, but rather reinforces it. Fulvic acid increases the attenuation of lead in the subsurface by enhanced sorption to clay materials as well as precipitation.

The chemical interactions that occurred between the clay, lead, and fulvic acid could not be determined from the data collected in this experiment. Figure 10 shows and describes proposed interactions that explain the collected data. It is unlikely that only one of these interactions is fully responsible for the observed results; more than one reaction may be occurring simultaneously.



1. The sorption of fulvic acid on clay materials does occur. Both clay and fulvic acid possess many reactive sites that can interact. If the clay is saturated with a cation such as calcium, the fulvic acid may not be able to displace it. Therefore, this reaction is probably controlled by competitive ion exchange. This was observed in the sorption of fulvic acid on calcium montmorillonite.
2. It is very likely that the sorption of lead on fulvic acid does occur. Both substances are reactive.
3. The sorption of lead on clay materials does occur. The cation exchange capacity of the clay material is a good indicator of the quantity of lead that will be sorbed. There is evidence that lead is strongly sorbed to clay and the reaction occurs quickly. Literature suggests that this reaction is reversible and controlled by competitive cations.
4. In this reaction, the fulvic acid preferentially binds to the clay material and sorbs lead. This reaction would explain many of the observations from this experiment. This reaction may occur at low lead concentrations. However, the literature indicates that lead can out compete organics for sorption sites. Therefore, the most probable reaction is number six.
5. This reaction could explain the precipitation of lead and fulvic acid. The addition of lead to a fulvic acid solution caused the solution to become cloudy. Long chains of fulvic acid bound to one another by lead ions may be responsible for this observation.
6. This reaction provides the most likely explanation for the observed data. The lead ion shares its charge between the clay material and the fulvic acid molecule. Because fulvic acids molecules have many reactive sites they can react with lead in solution enhancing the removal of lead from solution.

Figure 10. Proposed chemical interactions.

## 12 Conclusions and Recommendations

The research investigated one parameter—of many mechanisms—that affects the transport of lead in the subsurface. Fulvic acid was chosen as a variable likely to decrease attenuation of lead in the subsurface since past research indicated that fulvic acid increases the solubility of lead, and is correlated with increased lead concentrations in leachate.

Contrary to expectations, it was observed that the sorption of lead on clay materials was enhanced by the presence of fulvic acid. Fulvic acid was able to occupy more of the available sorption sites on kaolinite than on calcium montmorillonite. The data collected supports the theory that fulvic acid molecules are not able to effectively displace multivalent cations, such as calcium, from sorption sites. Fulvic acid sorption to clay materials was enhanced by increasing concentrations of lead in solution. The evidence suggests that, as the lead concentration increases, the sorption of fulvic acid will also approach a constant value.

Lead poses a unique risk to human health because of its wide use in society today. Without a complete understanding of soil attenuation, biotransformation rates, transport rates, and stabilization mechanisms of pollutants, the full protection of the environment is not possible. This research investigated only one parameter affecting the transport of lead in the subsurface; data from this study indicates that the presence of fulvic acid enhances the attenuation of lead in the subsurface. However, these results should not be used in isolation, without accounting for the many other parameters that may also affect the movement of lead in the subsurface. The financial and public image damage resulting from improperly disposed of lead-based paint materials far outweigh the extra expense associated with the proper management of the material. It is recommended that research continue to identify and analyze other variables that affect lead mobility to protect groundwater sources and human health.

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